GEORGIA INSTITUTE OF TECHNOLOGY — OFFICE OF CONTRACT ADMINISTRATION

PROJECT ADMINISTRATION DATA SHEET

[X] ORIGINAL [ ] REVISION NO. _____

Project No. E-16-606 (Continuation of E-16-627) GTRI/~~GXX~~ DATE 9 / 22 / 83

Project Director: Dr. J. I. Jagoda School/~~XXX~~ Aerospace Engineering

Sponsor: U. S. Environmental Protection Agency
Washington, D.C.

Type Agreement: Grant No. R-808953-02-0

Award Period: From 8/26/83 To ~~8/25/84~~ 12-25-84 (Performance) _____ (Reports)

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Funded: $		$ $63,162*

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Title: "Soot Formation in Gaseous Diffusion Flames"

ADMINISTRATIVE DATA OCA Contact John W. Burdette X4820

1) Sponsor Technical Contact:

Donald F. Carey
Science Review Administrator (RD-675)
Environmental Protection Agency
Washington, D.C. 20460

(202) 382-5744

2) Sponsor Admin/Contractual Matters:

Robert Woodside
Grants Specialist (ORGC/HQ)
Grants Administration Division
Environmental Protection Agency
Washington, D.C. 20460

Defense Priority Rating: _____ Military Security Classification: _____

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RESTRICTIONS

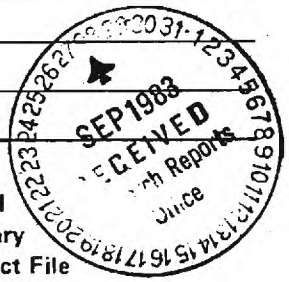
See Attached EPA Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with _____

COMMENTS:

*This amount represents the budget period 8/26/83-8/25/84. Total value of the Grant is $168,994 (including E-16-627).



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SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date June 5, 1985

Project No. E-16-606 School ~~AAAX~~ Aerospace Engineering

Includes Subproject No.(s) N/A

Project Director(s) Dr. J.I. Jagoda (Jechiel) 1949 GTRC / ~~GIT~~

Sponsor U.S. Environmental Protection Agency

Title "Soot Formation in Gaseous Diffusion Flames"

Effective Completion Date: 12/25/84 (Performance) 12/25/84 (Reports)

Grant/Contract Closeout Actions Remaining:

- [ ] None
- [ ] Final Invoice or Final Fiscal Report
- [ ] Closing Documents
- [X] Final Report of Inventions
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FORM OCA 69.285

Soot Formation in Gaseous Diffusion Flames

5th 6-Monthly Progress Report

Submitted to the

United States Environmental Protection Agency

Under Contract # R 80895 3010

by

J. I. Jagoda, Principal Investigator

School of Aerospace Engineering

Georgia Institute of Technology

February 1984

I. Work completed during the past reporting period.

The work carried out during the past reporting period concentrated on the effect on the mechanism of soot formation of traces of oxygen added to the fuel of a propane-air diffusion flame. The effects of these oxygen traces on the physical properties of the soot spheroids and their agglomerates were determined using the probe and transmission electron microscopy method and the laser light scattering and absorption techniques respectively. These findings were used to explain the increase in sooting of oxygenated diffusion flames previously observed in global sootiness measurements. In particular, it was established that the increase in soot formation rate due to the presence of oxygen in the fuel exceeded that predicted purely from the resulting increase in flame temperature. A homogeneous catalysis of the fuel pyrolysis by the oxygen is, therefore, indicated. This was shown to result in larger soot spheroids and some increase in agglomeration.

This work has been submitted for presentation at and inclusion in the proceedings of the 20th Symposium (International) on Combustion to be held in Ann Arbor, MI, this August. Since this paper includes all findings reportable for the past reporting period and since the bulk of the work included in this manuscript was actually carried out during the past six months, a copy is included with this progress report and details are not repeated here.

Apart from the experimental work described above, a theoretical effort continued to improve and refine the buoyancy model. The conservation of mass and momentum were applied to this one-dimensional model, and the perfect gas equation of state was used to relate density changes with height to the known temperature variation with height. Again,

pressure was assumed constant at any given height, but it was allowed to vary with height due to gravity forces. A system of first order differential equations for the fuel and oxidizer velocities were obtained which were then solved numerically for various cases using the fourth order Runge-Kutta technique. The fuel velocity was then used to obtain residence times as a function of height above the burner.

The temperature data for ethylene/air flames obtained by Kent, et al.(1981) was used in the model to obtain theoretical velocities to compare with the experimentally obtained velocities. This study was limited by the lack of experimental temperature data for low heights (less than 20mm) and for large distances from the burner centerline where the oxidizer is relatively cool. The best fit to the velocity data occurred for centerline fuel temperature (T_{max} = 1320^{o}K at y = 20 mm) and a reasonable oxidizer temperature variation (T_{max} = 865^{o}K at y = 110 mm). The residence times obtained with this temperature variation were about twice those obtained previously with the constant temperature model. This is primarily due to the lower velocities obtained close to the burner when temperature variations are taken into account.

II. Activities planned for the next reporting period.

During the next reporting period the improved model for computing vertical gas velocities in the presence of thermal expansion and buoyancy will be applied to our experimental results.

On the theoretical side, recent measurements have indicated interesting trends in the vicinity of the flame tip. Soot aggregate sizes have

been observed to reach a maximum diameter and then remain essentially constant. Further measurements will be carried out near the flame tip, where soot burnout may be expected to commence. An extensive search of the literature has shown that very little is known about the controlling processes in this part of the flame. Since, however, the burnout process is essential to the determination of the final sootiness of any diffusion flame, more detailed measurements will be carried out near the flame tip.

Further efforts will also be expended on improving our temperature measurements and comparing them with those used by others in similar flames. Time permitting, the effect on the soot formation processes of adding ion-producing additives and aromatic compounds to the flame will be investigated.

Finally, the results obtained from all measurements will be compared with available global observations from the literature. The various theories put forward to explain the global results will be compared with our detailed "in flame" measurements to assess their validity. A number of new concepts are also being considered which, it is hoped, will expand existing knwledge of the fundamentals of soot formation in diffusion flames.

The paper entitled "The Effect of Temperature on Soot Formation in Laminar Diffusion Flames", submitted to Combustion Science and Technology has been accepted for publication. The final edited version of this manuscript will be forwarded to the monitor shortly. A decision on the paper submitted for the 20th Symposium on Combustion, a copy of which is enclosed, is expected within the next 4-6 weeks.

III. Reference.

Kent, J. H., Jander, H. and Wagner, H. G. (1981). Soot Formation in a Laminar Diffusion Flame. 18th Symposium (International) on Combustion, Waterloo, pp. 1117-1126.

Submitted for the 20th Symposium (International) on Combustion

The Effect on Soot Formation of Oxygen in the Fuel of a Diffusion Flame

by

Wey, C., Powell, E. A. and Jagoda*, J. I.

School of Aerospace Engineering

Georgia Institute of Technology

Atlanta, Georgia 30332

Subject Matter: Soot Formation

Fires

Air Pollution

* Author to whom all correspondence should be addressed

Abstract

This study deals with the effect on the soot formation process of the addition of small quantities of oxygen to the fuel of a propane air diffusion flame. Electron microscopy of extracted samples and 'in situ' laser light scattering techniques were used to determine the soot volume fractions, soot aggregate diameters and number densities as well as spherule sizes. From these the local degrees of agglomeration were obtained. It was shown that while the basic processes of soot formation in a diffusion flame are unchanged by the addition of small quantities of oxygen to the fuel, the soot loadings are increased far beyond what would be predicted by considering the resultant rise in temperature only. The increased rate of formation of the pyrolysis products by the catalytic action of the oxygen results in the production of larger soot spherules. These, along with an accelerated agglomeration account for a more rapid growth of the soot aggregates in the oxygenated flames. The maximum soot aggregate diameters are, however, equal in the flames with and without oxygen in the fuel. Once this maximum diameter has been attained, any further increase in total soot loading in the oxygenated flames is due to spreading of the soot carrying region towards the center of the flame. Within the experimental accuracy, the addition of traces of oxygen to the fuel did not result in a noticeable change in the aggregate number densities near the flame front.

Introduction

Smoke has been recognized as the major cause of fatalities in building fires [1] and as a source of atmospheric pollution generated by many practical combustion devices. Futhermore, the increased wall heating due to radiative heat transfer from the solid particles results in materials design problems in many combustors. For these reasons a number of investigations have been carried out into the mechanisms of soot formation during the combustion of hydrocarbons. Many of their findings have been summarized in a number of excellent review articles [2,3,4,5,6,7]. Earlier work has concentrated on soot formation in premixed flames since these flames are more easily controllable. Most natural combustion processes, however, occur, at least partially, in the form of diffusion flames. Some recent investigations have, therefore, concentrated on soot measurements in diffusion flames [8,9,10].

The general steps leading to soot formation such as nucleation, coagulation, aggregation and surface growth and their chronological order are now quite well established. The details of the various processes involved in soot formation are, however, yet to be determined. A number of observed global effects of different combustion parameters on the amount of soot produced are also yet to be explained in terms of the individual steps of soot formation. The effect of traces of oxygen in the fuel of a diffusion flame is one example, which will be addressed in this study. The interest in such detailed investigations into the role of a single combustion parameter on the process of soot formation is not confined to the explanation of that one effect. Many chemical and physical processes work together to produce relatively large carbon particles from small hydrocarbon molecules, radicals or ions within a few milliseconds. The only way this complex interplay of effects can be elucidated is by determining how each of the various parameters influences the complex formation processes leading to soot.

Chakraborty and Long [11] using global determinations of total soot formed showed that the addition of up to 17% of stoichiometric oxygen to ethylene or ethane in diffusion flames causes a marked increase in the amount of polycyclic aromatic hydrocarbons and soot formed. The authors suggested that the additional oxygen causes an increase in temperature resulting in an accelerated formation of acetylene leading to soot by polymerization and dehydrogenation. Similar global observations were made by Wright [12] for a number of saturated and unsaturated hydrocarbon fuels. This author concluded that there was no evidence that the higher soot formation rates are due to higher temperatures in the pyrolysis zone. His conclusions were based on the fact that additions of inerts of different heat capacities had no noticeable effect on the soot formation rate. He explained the increase in sooting by a catalytic effect of the oxygen on the polymerization reactions which lead to the increased production of large molecular weight soot precursors. Others [13,14] also found a decrease in sooting height (i.e., an increase in sooting tendency) when traces of oxygen were added to a variety of fuels in diffusion flames. They explained this effect by a dehydrogenation of the fuel by oxygen in the pyrolysis zone and used this observation to support their conclusion that the pyrolysis of the fuel is the crucial step in soot formation in diffusion flames.

The effect of traces of oxygen in the pyrolytic decomposition of hydrocarbon fuels had been documented in earlier works. Smith and Gordon[15] suggested that small quantities of oxygen entering the diffusion flame through the quenched annulus near the burner lip play an important role in the decomposition of methane. Engel et al. [16] reported a considerable increase in the pyrolytic decomposition in a combustion bomb due to oxygen traces in a variety of hydrocarbons, including propane, for temperatures up to 600°C. Similar effects were obtained by Storch[17] using ethylene. Finally, Walsh [18] and Glassman [19] suggested a number of chemical mechanisms by which oxygen takes part in the decomposition of hydrocarbon fuels.

It is the purpose of this study to determine the effect of the additions of small amounts of oxygen to the fuel of a propane air diffusion flame. It has been established [8,9,10] that in pure fueled diffusion flames soot nucleation occurs near the flame front while particles grow by coagulation, aggregation and surface growth as they move towards the burner center. Soot spherule and aggregate diameters, aggregate number densities and soot volume fractions were measured to determine the possible effects of traces of oxygen in the fuel on the above outlined formation steps. The effects of temperature changes due to the additional oxygen on the soot production process were also investigated. It is anticipated that the obtained results will help in furthering the understanding of the detailed processes involved in the formation of soot.

Experimental Techniques

Burner

A Parker Wolfhard burner, similar to the one used in previous investigations [8,9,10,20] was used in this study. The burner consists of three parallel slots 51 mm in length. The outer slots, which carry the oxidizer, are each 16 mm wide, while the inner fuel slot has a width of 5 mm. This burner was selected as it produces a pair of vertical flat flame sheets which eliminates the need to deconvolute the absorption signal as is necessary in cylindrically symmetrical flames[11, 21]. Equal cold fuel and oxidizer velocities of 3 cm/sec as used in this investigation result in a stable, somewhat underventilated flame. The burner is surrounded by a nitrogen carrying jacket to exclude drafts and to prevent the formation of end-flamelets. Screens placed near the tip of the flame result in further flame stabilization. The burner is water cooled in order to permit steady operation over an extended period of time. The burner assembly is translatable in the vertical and horizontal directions to enable measurements to be carried out in all parts of the flame without disturbing the optical system. All gas flow rates were measured using calibrated rotameters.

Diagnostics

Soot consists of agglomerates of essentially spherical particles or spherules. It is formed in a nucleation step followed by coagulation (the agglomeration of two or more nuclei followed by heavy surface growth which results in larger spherical particles), pure surface growth and agglomeration into clusters of soot spherules. In order to quantify the effects of the various combustion conditions on each of the steps in the formation process it is essential to be able to differentiate between the soot spherules and their agglomerates. To this end electron microscopy and laser optical techniques have been used in a complimentary fashion in this study.

Soot samples were extracted from various locations in the flame and spherule diameter distributions determined using transmission electron microscopy. The electron micrographs also showed extensive agglomeration of the spherules. This, however, is due mostly to agglomeration during sample collection, and is not representative of the degree of agglomeration in the flame. The agglomerate properties were, therefore, measured 'in situ' using simultaneous laser light scattering and absorption. This method also permits the determination of local soot volume fractions in all parts of the flame.

This optical technique, which was pioneered by D'Alessio et al. [23] has been described previously [22,23] and will, therefore, only be outlined here. The beam from a 4 watt argon ion laser operating at 514.5 nm is focused into the test section in the flame using a 50 cm focal length lens and passes along the flat flame sheet onto a photomultiplier which measures the intensity of the transmitted light. A second photomultiplier is used to monitor the intensity of the beam scattered at 90^{o}. A system of lenses and apertures restricts the solid angle over which scattered light is collected and limits the size of the test volume to 100 microns cubed. Direct radiation from the flame which passes the monochromator and narrow band pass interference filter is eliminated by placing a chopper in the incident beam and passing the output from the photomultipliers through a phase sensitive detector which amplifies only the signal originating from the

laser beam. The absorption and scattering signals are passed through an A/D converter. An HP 2100 computer is used to reduce the data and store the results on disc.

The Mie theory in the Rayleigh approximation as detailed by Kerker [24] was used to analyze the data. The scattering cross-sections, C_{sca}, of the soot aggregates were determined from the incident and scattered intensities of the laser beam while the extinction coefficients, K_{ext}, were determined from the incident and transmitted intensities (Beer - Lambert Law). The mean scatterer diameters (D) and their number densities (N) were obtained from the scattering cross-sections and extinction coefficients, while the extinction coefficients by themselves yielded the soot volume fractions. The details of the mathematical relationships used are listed in Refs. 21 and 22 and others, and will, therefore, not be repeated here. The determination of K_{ext} is less precise than that of C_{sca} since the absorption measurements integrate over the entire length of the flame and are thus influenced by any possible deviation from perfect flame flatness or the existence of small end flamelets. Since N is proportional to the square of K_{ext} while D is a function of only the cube root of K_{ext}, the determination of the number densities may be expected to be less accurate than that of the agglomerate dimensions.

The values of C_{sca} obtained depend on a number of geometrical parameters of the scattering system. Rather than measure these parameters the system was calibrated [22,23] using pure nitrogen and methane whose scattering cross-sections were calculated [25,26] and compared with those quoted by Rudder and Bach [27] for the respective wavelengths.

In the absence of any information about the form of the agglomerate size distributions, a monodisperse distribution was assumed. Furthermore, the Rayleigh theory assumes spherical scatterers whose $D \ll \lambda$. These criteria are not always strictly observed, but it can be shown that for particles of 100 nm diameter the error introduced is only 10%[21]. Lastly, the soot aggregates are not spherical and only "equivalent diameters" could, therefore, be established.

Both scattering and extinction measurements had to be averaged over excursions of about 5% in most parts of the flame. In areas of steep soot concentration gradients, these fluctations due to small movements of the flame were somewhat bigger, but the results were, nevertheless, reproducible.

In summary, laser scattering was used to determine the agglomerate properties while electron microscopy yielded spherule dimensions. In addition the temperature distributions in the flames were measured using Pt, Pt-13%Rh thermocouples with a 125 micron diameter junction. Conductive losses were minimized by introducing the leads parallel to the flame sheet. Since only relative temperatures are of interest here, the thermocouple results were not corrected for radiative losses.

Results and Discussion

Three propane-air diffusion flames were investigated. Flame A consisted of pure propane fuel while 10% and 20% oxygen by volume were added to the fuel of Flames B and C respectively. This corresponds to a molar equivalence ratio of .02 and .04 for Flames B and C. The calculated adiabatic flame temperatures were 2265°K for Flame A, 2283°K for Flame B and 2305°K for Flame C.

The changes in the flame shape caused by the addition of oxygen to the fuel can be illustrated by comparing the temperature profiles for the three flames shown in Fig. 1. There is a slight increase (about 2% per 10% of oxygen added) in the maximum temperature and a narrowing of the flame with increased oxygen in the fuel. Furthermore, it has been observed that in the lower part of the flame the temperature at the flame front remains constant, while that in the flame center increases with height. Closer to the flame tip the flame front temperature decreases somewhat with height above the burner (probably due to radiative heat losses from the heavier soot loadings), while that near the flame center remains constant. Inspection of Fig. 1 shows that the temperature characteristics associated with the upper part of the flame occur earlier with

Fig 1

increasing oxygen content in the fuel. Furthermore, for Flame C the temperature maximum begins to move noticeably towards the burner center above 40mm from the burner mouth indicating that one is closer to the flame tip. This conclusion was confirmed by a shortening of the visible part of the flame with increasing oxygen content in the fuel but constant total flow rate.

The measured soot volume fractions are plotted versus distance from the burner center for different heights above the burner in Fig. 2. For all three flames the maximum soot loadings, which lie well within the fuel side of the flame, increase with height above the burner. The same holds true for the total soot volume fractions (i.e., areas under the soot volume fraction curves) except at 50 mm above the burner for Flame C which is relatively close to the flame tip where the soot loading has leveled off. When comparing soot volume fractions at given heights in the three flames, it is seen that the soot loadings increase with oxygen content in the fuel. The notable exception occurs, once again, at 50 mm above the burner in Flame C where soot burnout may be expected to have commenced. A glance at the temperature plot (Fig. 1) indicates that the actual tip of Flame C lies above 50mm over the burner. Previous investigations [28], however, have shown that the initial point at which soot pierces through the flame occurs below the flame apex. Furthermore it may be observed that to some extent in Flame B and more so in Flame C the soot loading near the center increases considerably with height above the burner.

Some workers have previously suggested [11] that the increase in global soot formation rate due to traces of oxygen in the fuel of a diffusion flame may be due to a resultant increase in flame temperature. When comparing the temperature and soot loading increases due to the addition of oxygen to the fuel with those obtained by increasing the temperature through a reduction of the inert nitrogen content in the oxidizer [20] it becomes apparent that the observed increase in sooting due to the addition of oxygen to the fuel cannot be ascribed to a thermal effect only. Comparing Flames A

and C, for example, shows, typically, a doubling in total soot mass loading for an increase of only 60°K in the flame front temperature. A pure temperature effect [20], however, produced only a tripling in soot loading for an increase of 210°K in the flame front temperature. Clearly the oxygen in the fuel has a soot enhancing effect over and above any possible increase caused by higher temperatures.

Figure 3 shows the horizontal distributions of aggregate diameters for different heights above the burner for the three flames. Generally the regions of maximum soot loading also correspond to those in which soot agglomerates of the largest diameters are found. The soot aggregate diameters increase with height above the burner until they level off for all flames at a diameter of approximately 120 nm in the upper part of the flame. A small decrease in diameter is observed near the tip of Flame C. As the oxygen content in the fuel is increased the aggregate diameters increase more rapidly and reach their maximum value at lower heights in the flame. Furthermore, large aggregates are observed near the central axis at lower heights in the flame. The positions of maximum aggregate diameters follow the flame shape. This is particularly noticeable in Flame C where the highest measurements are closest to the flame tip.

The aggregate number density distributions are shown in Fig. 4. As mentioned previously, the values of the number densities are least reliable. Since the absorption near the burner center was relatively small and was possibly influenced by large polycyclic aromatic hydrocarbons in the preheating zone, the number densities are only plotted up to 1½ mm from the burner center. The number densities are highest near the flame front and decrease due to agglomeration as the aggregate diameters increase towards the burner center. Addition of oxygen to the fuel does not seem to affect the number density distributions other than a slight horizontal displacement which is brought about by changes in the flame shape.

The variations of the spherule diameters with height above the burner for the three flames are shown in Fig. 5. Due to the low spatial resolution of the sampling technique,

only one average sample per height could be obtained. The mean spherule diameters increase with height above the burner for all three flames except near the tip of Flame C where some burnout may have occurred. An increase in the oxygen content in the fuel results in larger spherules as may be expected since more pyrolysis products are available for surface growth.

In order to obtain an indication of the degree of agglomeration in the soot clusters at different heights in the flames, the volumes calculated from the maximum "equivalent diameters" of the aggregates were divided by those obtained from the mean diameters of the spherules at the same height. Because of the irregular shapes of the soot aggregates, this results in very approximate values only. Table I shows that the degree of agglomeration increases with height above the burner until a limiting value of about 200 is reached. As the oxygen content in the fuel is increased the agglomeration process accelerates, although the maximum degree of agglomeration is the same for all three flames, within the experimental accuracy, with the possible exception of the top position in Flame C.

Table 1

Finally, from the similarities of the overall shapes of the soot parameter (F_v, D, N) distributions obtained with and without the addition of oxygen to the fuel, it can be concluded that the fundamental mechanisms of soot formation in diffusion flames [8,9,10] are maintained in the presence of small quantities of oxygen in the fuel. However, trace oxygen in the fuel increases the rate of surface growth and agglomeration because of the larger amounts of pyrolysis products available in the preheating zone.

Conclusions

The effect of the addition of small quantities of oxygen to the fuel of a propane air diffusion flame on the soot formation mechanism was investigated. Both 'in situ' optical and sampling techniques were used to determine soot volume fractions and soot aggregate and spherule properties. Thermocouple measurements indicated that the flame front

temperature increases were small for the amounts of oxygen added and that the resulting flames were somewhat narrower and shorter indicating an acceleration of the combustion process. The addition of a relatively small molar fraction of oxygen to the fuel results in an increase in soot loading in the flame considerably in excess of that expected purely due to the increase in temperature. Soot aggregates, whose diameters increase with height in the flames, grow more rapidly in the oxygenated flames but reach a common maximum size in all three flames. These maximum diameters are reached at lower heights with increasing oxygen content in the fuel. Once the largest agglomerate size has been attained, further increases in soot loading in the flame are due to an extension of the sooty zone towards the burner center. The increased growth rate of the aggregate diameters is due in part to an increase in the size of the spherules which make up the agglomerates and partly to an accelerated agglomeration process. The agglomerate number densities in the vicinity of the flame front appear unchanged, within the experimental accuracy, by addition of oxygen to the fuel.

In summary it may be concluded that the soot formation mechanisms determined for pure diffusion flames remain valid when small quantities of oxygen are introduced into the fuel. The trace oxygen increases the pyrolysis rate in the preheating zone by homogeneous catalysis. This results in an increased rate of soot formation which is reflected in a more rapid growth of soot agglomerates and a spreading of the soot carrying zone. The agglomerate maximum diameters, however, are limited in all three flames to about 120 nm. The larger agglomerate growth is caused by the increased agglomeration of somewhat larger spherules. Data obtained from the highest measurement plane in the most oxygenated flame indicate the beginning of soot burnout prior to reaching the flame tip. Further work is necessary to increase our understanding of the steps responsible for soot burnout near the apex of diffusion flames.

Acknowledgement

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References

1) Neville, A.E.: "America Burning," Report of the National Commission on Fire Prevention and Control, pp 61-69, 1972.

2) Wagner, H. G.: 18th Symposium (International) on Combustion, pp 3-19, The Combustion Institute, 1981.

3) Haynes, B.S. and Wagner, H.G.: Prog Energy Combust. Sci, Vol 7, pp 229-273, 1981.

4) Lahaye, J. and Prado, G.: Chemistry and Physics of Carbon (Walker, P. L., Ed), Vol 14, pp 168-294, Marcell Dekker, 1978.

5) Homan, K. H.: Comb. Flame, Vol 11, pp 265-287, 1967.

6) Howard, J. B. and Kausch, Jr., W. J.: Prog. Energy and Combust. Sci., Vol 6, pp 263-276, 1980.

7) Calcote, H. F.: Comb. Flame, Vol 42, pp 215-242, 1981.

8) Haynes, B. S. and Wagner, H. G.: Ber. Bunsenges Phys. Chem., Vol 84, pp 499-506, 1980.

9) Kent, J. H., Jander, H. and Wagner, H. G.: 18th Symposium (International) on Combustion, pp 1117-1126, The Combustion Institute, 1981.

10) Kent, J. H. and Wagner, H. G.: Comb. Flame, Vol 47, pp 53-65, 1982.

11) Chakraborty, B. B. and Long, R. R. : Comb. Flame, Vol 12, pp 469-476, 1968.

12) Wright, F. J.: Fuel, Vol 53, pp 232-235, 1974.

13) Schug, K. P., Manheimer-Timnat, Y., Yaccarino, P. and Glassman, I.: Comb. Sci. and Tech., Vol 22, pp 235-250, 1980.

14) Glassman, I.: "Phenomenological Models of Soot Processes in Combustion Systems," Princeton University, Dept. of Mechanical and Aerospace Engineering Report 1450, 1979.

15) Smith, S. R. and Gordon, A. S.: J. Phys. Chem., Vol 60, pp 759-763, 1956.

16) Engel, J., Combe, A., Letort, M. and Niclause, M.: Rev. de L'Inst. Franc. du Petr., Vol 12, pp 627-644, 1957.

17) Storch, H. H.: J. Am. Chem. Soc., Vol 57, pp 2598-2601, 1953.

18) Walsh, A. D.: Trans. Far. Soc., Vol 42, pp 269-284, 1946.

19) Glassman, I.: "The Homogeneous Oxidation Kinetics of Hydrocarbons: Concisely and with Application," Plenary Lecture Annual Meeting of the Combustion Institute, Sezione Italiana, Torino, Italy, June 1979.

20) Wey, C., Powell, E. A. and Jagoda, J. I.: "The Effect of Temperature on the Sooting Behavior of Laminar Diffusion Flames," submitted to Comb. Sci. and Tech., 1983.

21) Santoro, R. J., Semerjian, H. G. and Dobbins, R. A.: Comb. Flame Vol 51, pp 203-218, 1983.

22) Jagoda, J. I., Prado, G. and Lahaye, J.: Comb. Flame, Vol 37, pp 261-274, 1980.

23) D'Alessio, A., DiLorenzo, A., Micera, G. and Beretta, F.: 2^{o} Simposio di Dinamica della Reazioni Chimiche, Padova, pp 147-156, 1975.

24) Kerker, M.: The Scattering of Light and Other Electromagnetic Radiation, pp 31-39, Academic Press, 1969.

25) Penney, C. M.: J Opt. Soc. Am., Vol 59, pp 34-38, 1969.

26) Müller-Dethlefs, K.: "Optical Studies of Soot Formation and the Addition of Organic Peroxides to Flames," Ph.D. thesis, Imperial College (University of London), pp 23-38, 1979.

27) Rudder, R. R. and Bach, D. R.: J. Opt. Soc. Am. Vol 58, No 9, pp 1260-1266, 1968.

28) Glassman, I. and Yaccarino, P.: Comb. Sci. and Tech. Vol 24, No 3 and 4, pp 107-114, 1982.

Table I: Approximate Degrees of Agglomeration for Flames A, B and C.

Height above	Flames		
burner (mm)	A	B	C
20	16	32	61
30	61	110	207
40	138	226	195
50	201	174	271

Figure Captions:

Fig. 1. Measured temperatures versus distance from the burner center for flames with 0% (A), 10%, (B) and 20% (C) of oxygen by volume in the fuel flow. (Height in mm's above burner: o 20, Δ 30, □ 40, × 45, + 50)

Fig. 2. Soot volume fractions versus distance from the burner center for flames with 0% (A), 10% (B) and 20% (C) of oxygen by volume in the fuel flow. (Height in mm's above burner: o 20, Δ 30, □ 40, × 45, + 50)

Fig. 3. Soot agglomerate diameters versus distance from the burner center for flames with 0% (A), 10% (B) and 20% (C) of oxygen by volume in the fuel flow. (Height in mm's above burner: o 20, Δ 30, □ 40, × 45, + 50)

Fig. 4. Soot agglomerate number densities versus distance from the burner center for flames with 0% (A), 10% (B) and 20% (C) of oxygen by volume in the fuel flow. (Height in mm's above burner: o 20, Δ 30, □ 40, × 45, + 50)

Fig. 5. Mean spherule diameters versus height above the burner for flames with: □ 0% (A), X 10% (B) and Δ 20% (C) of oxygen by volume in the fuel flow.

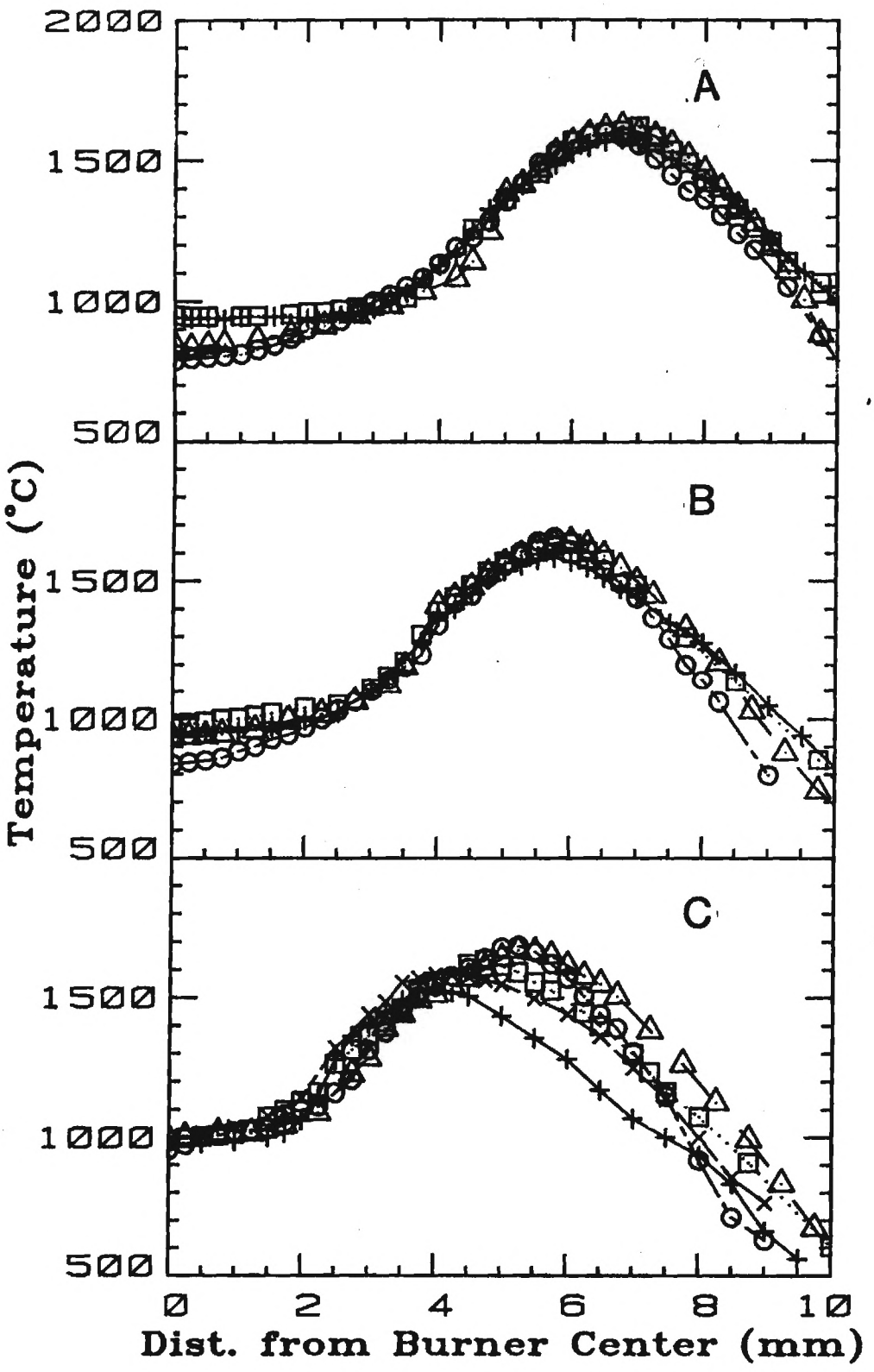
A
B
C
2000
1500
1000
500
Temperature (°C)
0
2
4
6
8
10
Dist. from Burner Center (mm)

Fig 1

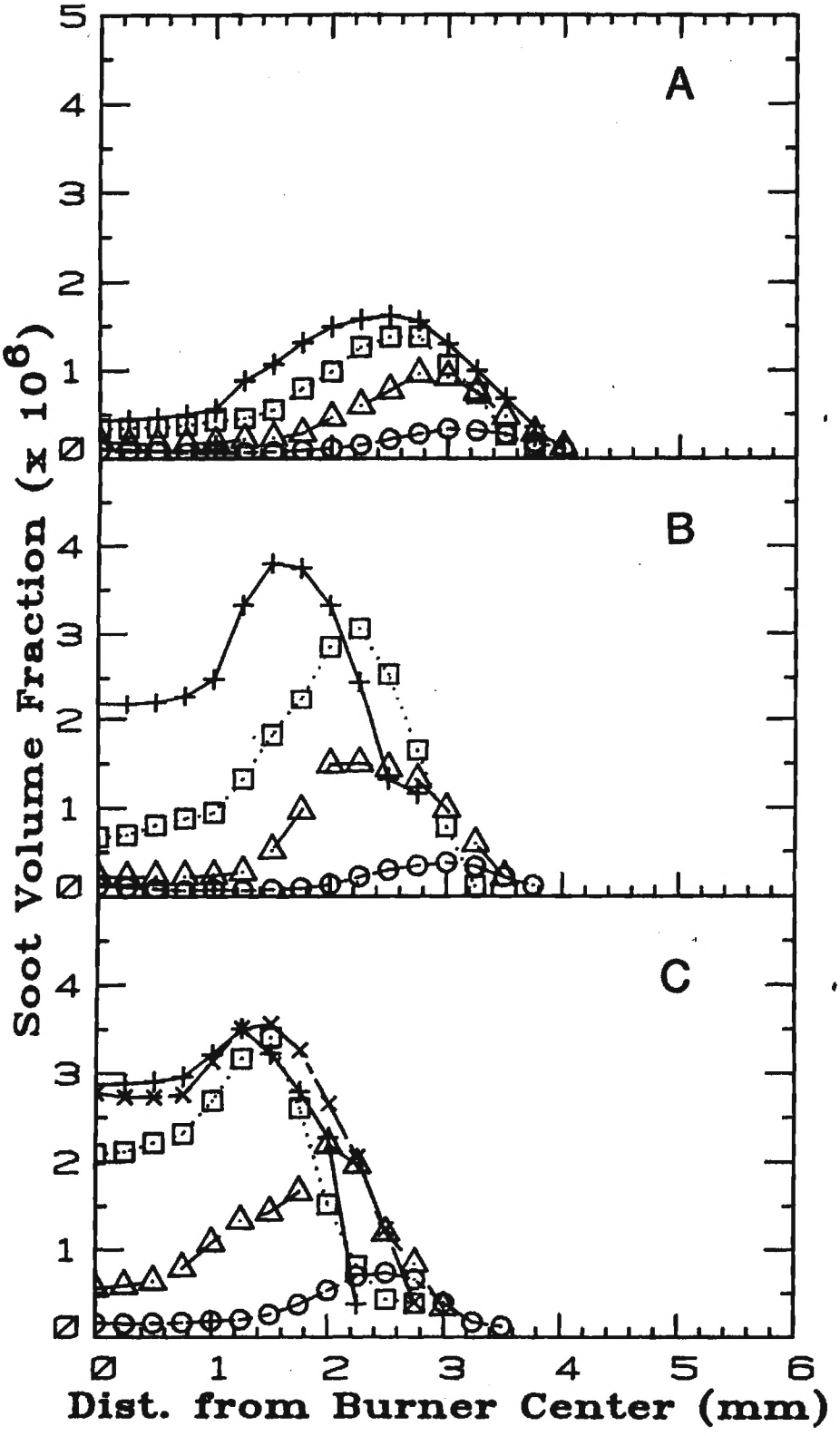
A
B
C
Soot Volume Fraction (x 10^6)
Dist. from Burner Center (mm)
0
1
2
3
4
5
6

Fig 2

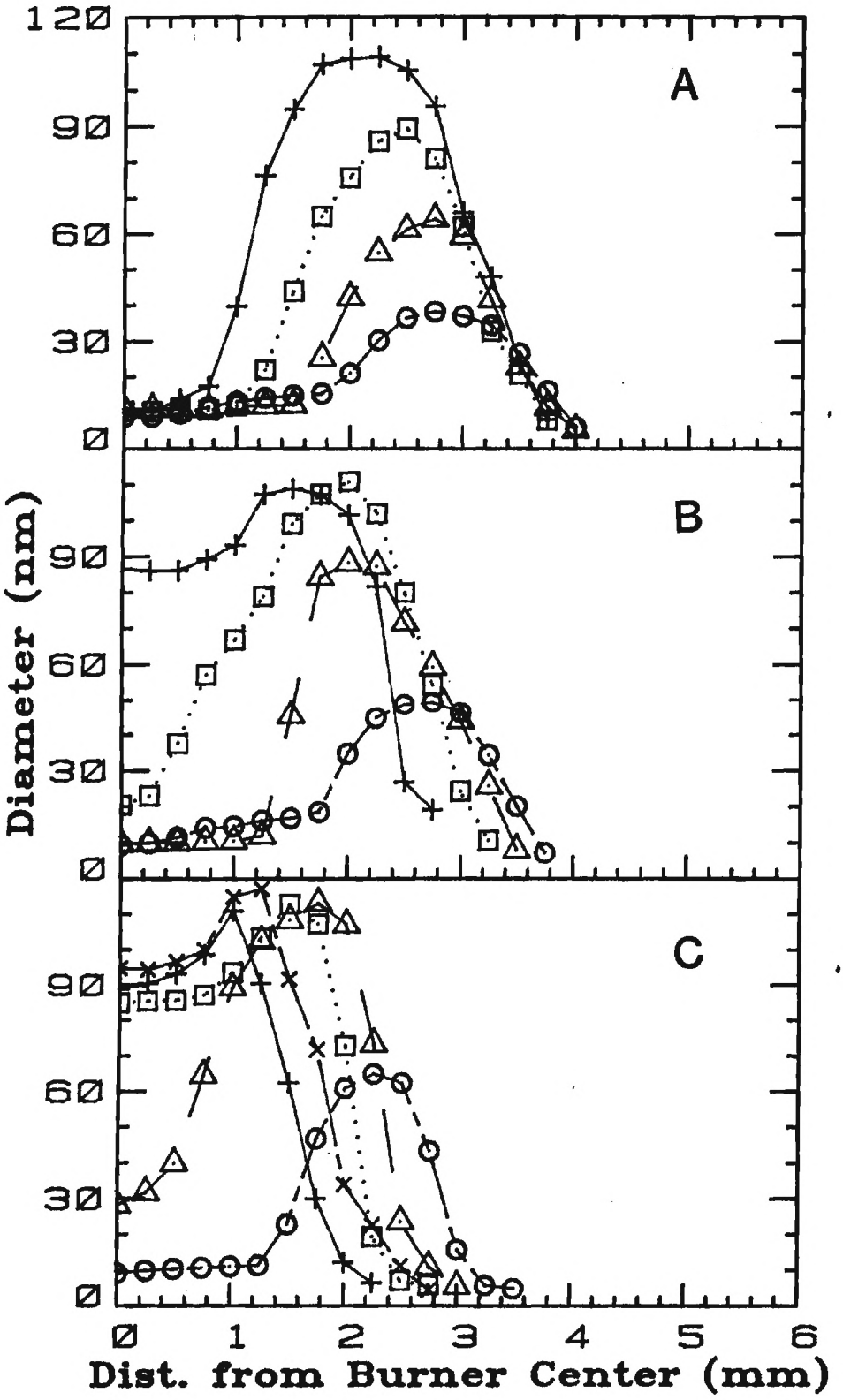
120
90
60
30
0
A
B
C
Diameter (nm)
0
1
2
3
4
5
6
Dist. from Burner Center (mm)

Fig 3

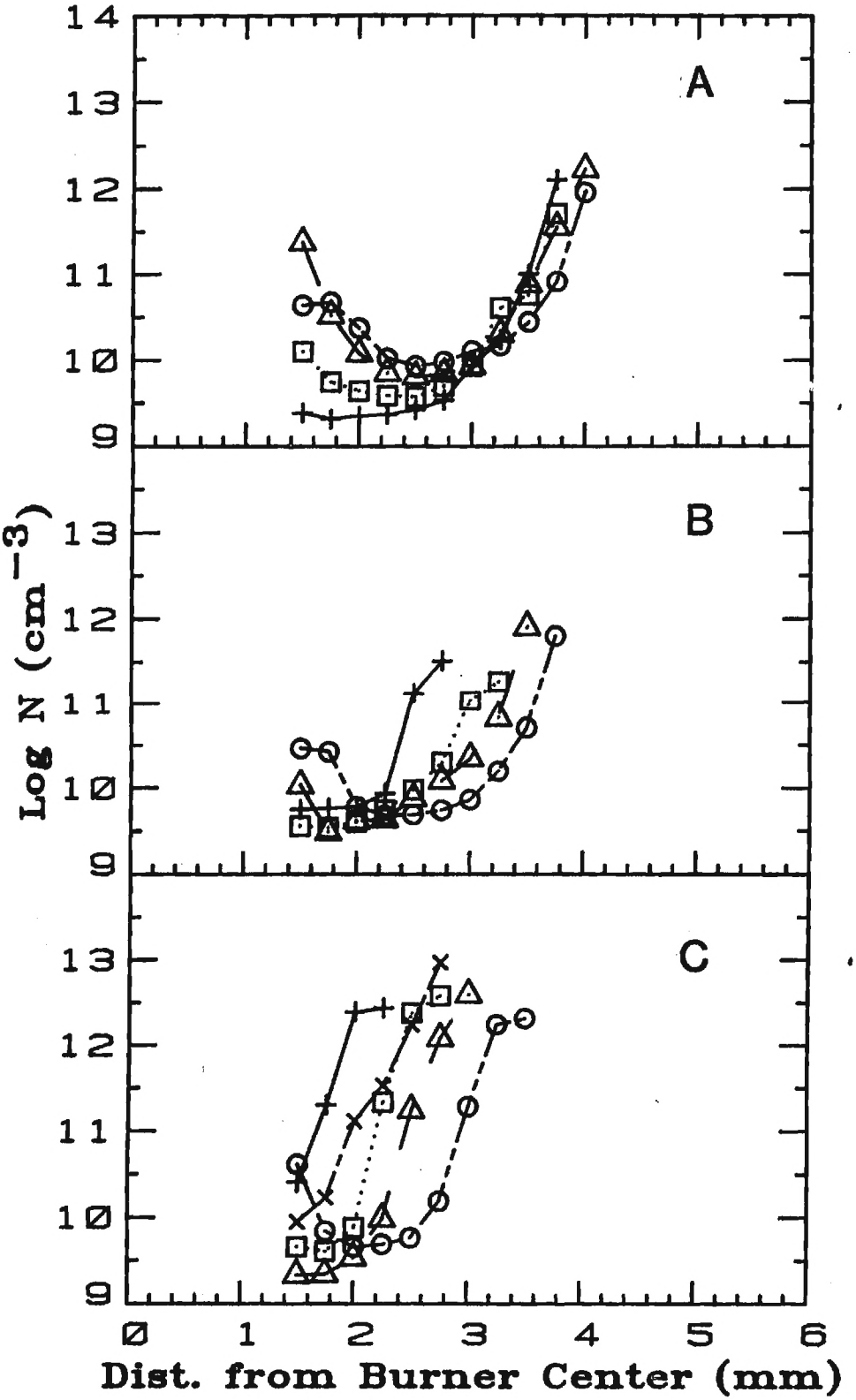

Fig 4

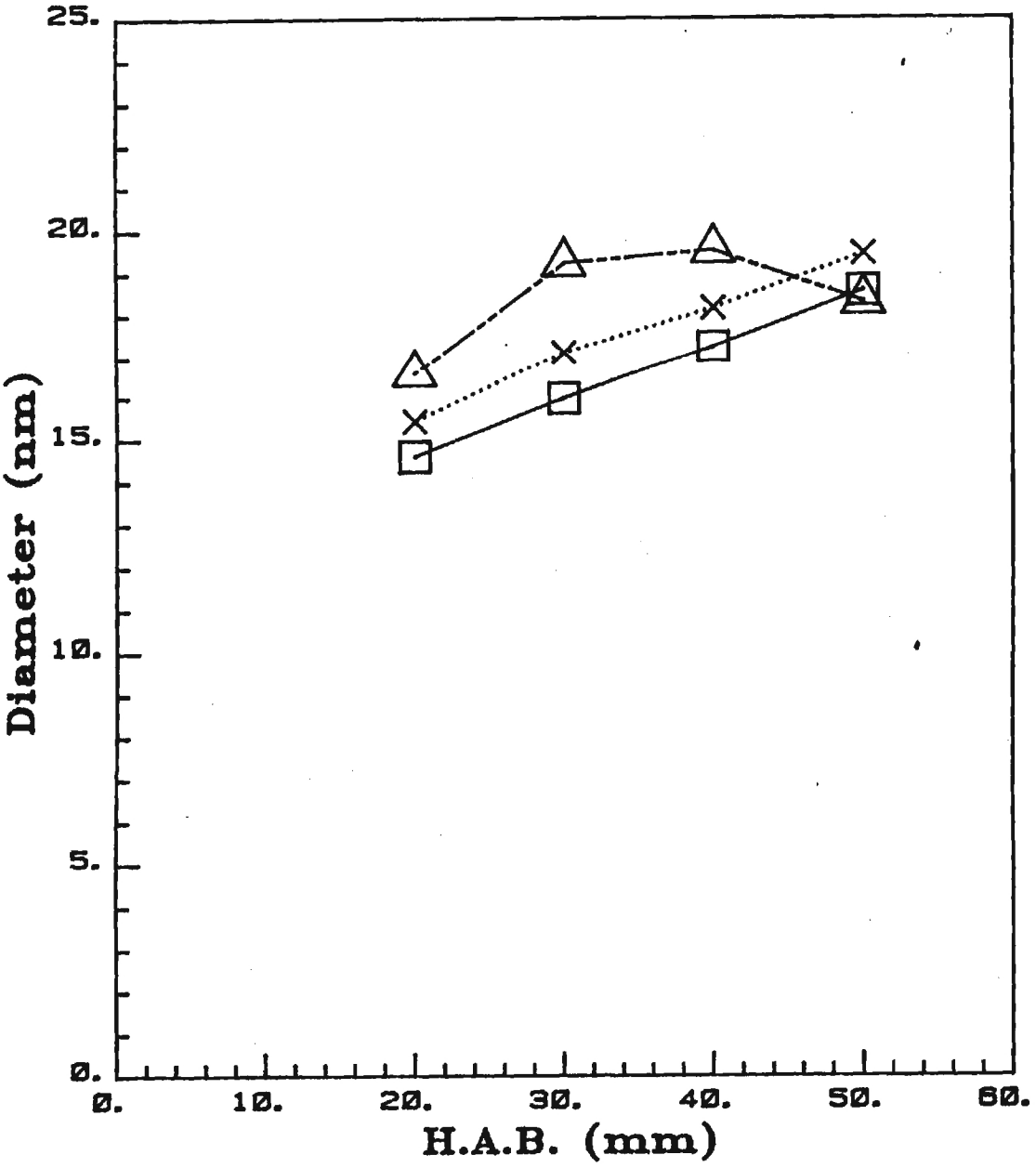

Fig 5

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The Effect of Temperature on the Sooting Behavior of Laminar Diffusion Flames

C. WEY, E. A. POWELL *and* J. I. JAGODA *School of Aerospace Engineering, Georgia Institute of Technology, Atlanta, GA 30332*

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Abstract—The effect of temperature on soot formation in a laminar propane diffusion flame was investigated. The temperature of the flame on a Parker Wolfhard burner was varied by adjusting the inert nitrogen content in the oxidizer flow. Local soot aggregate properties, such as aggregate diameters and their number densities as well as soot volume fractions were determined using simultaneous laser light scattering and extinction methods, while spherule diameters were obtained using sample extraction and transmission electron microscopy. Soot volume fractions and aggregate diameters were seen to increase with height above the burner, while the opposite trend was noted for aggregate number densities for the three flame temperatures investigated. Spherule diameters were seen to increase with height particularly in the early part of the flame. An increase in temperature resulted in a considerable increase in local soot volume fractions and aggregate diameters. Spherule size and degree of agglomeration also varied somewhat with temperature. Soot aggregate number densities, at least in the regions of noticeable soot loading, were found to be largely insensitive to changes in temperature. Heights above the burner were converted to residence times in the flame allowing for buoyancy. The mean rate of growth of the largest soot aggregates was found to be essentially independent of flame temperature, although the absolute soot particle diameters were larger in the hotter flames, resulting in an increase in sooting with temperature. An "effective growth residence time" was introduced to take account of the effects of temperature such that both total soot loadings and maximum soot diameter were the same for any given normalized time for all flame temperatures investigated.

I INTRODUCTION

The formation of soot during the combustion of hydrocarbons has become a matter of increasing concern over the last decade. Smoke has been recognized as the major cause of fatalities in building fires [see Neville (1972)] and as a source of atmospheric pollution generated by many practical combustion devices. Furthermore, the increased wall heating due to radiative heat transfer from the solid soot particles results in materials design problems in many combustors. With this in mind a great number of studies have been undertaken to further the understanding of the mechanisms responsible for the formation of soot under a variety of different combustion conditions. A number of excellent review papers have recently been published covering many aspects of the soot formation problem including Wagner (1981), Haynes and Wagner (1981), Lahaye and Prado (1978), Palmer and Cullis (1965), Homan (1967), Howard and Kausch (1980), and Calcote (1981). Since all building fires and many controlled combustion processes occur, at least partially, in the form of diffusion

flames, it was decided to further study the effect of various parameters on the formation of soot in laminar diffusion flames.

Glassman (1979), in a review of phenomenological models of soot formation, addressed the differences in the dependence of sooting behavior on temperature between premixed and diffusion flames. He reported that while for premixed flames an increase in flame temperature will result in a decrease in sooting tendency, a similar rise in temperature in diffusion flames will tend to increase the likelihood of soot being formed. These results were obtained using the concept of sooting height [see also Glassman and Yaccarino (1981)]. Similar observations in laminar diffusion flames were made by Dearden and Long (1968) who report an increased amount of soot collected with increasing flame temperature. This also sheds new light on results reported by Powell *et al.* (1979) on the effect of temperature on the sooting history of flames on wood and PVC. Here, post flame soot loadings and particle diameters were seen to increase with temperature when determined optically in the flue above their test chamber.

Glassman (1979) explained the differences in sooting trends with temperature in premixed and diffusion flames in terms of competing pyrolysis and oxidation reactions in the pre-sooting zones. In premixed flames, the rate of oxidation of soot precursors is accelerated more strongly by an increase in temperature than their formation via the pyrolysis reaction, leading to a reduction in soot. In diffusion flames, on the other hand, no oxidation takes place during preheating leaving only the pyrolysis reactions, which leads to an increase in sooting with temperature. Indeed, traces of oxygen which may diffuse into the pyrolysis zone of a diffusion flame tend to act as a homogeneous catalyst during pyrolysis and increase the sooting rate as was shown by Glassman and Yaccarino (1980) and Schug *et al.* (1980).

All the above observations were made in terms of global measurements such as sooting heights, amount of soot collected, etc. It would be interesting to extend these measurements to determine the effect of temperature on the properties of the soot particles as they are formed inside both premixed and diffusion flames. Soot consists of essentially spherical particles, or spherules, which agglomerate to form the soot agglomerates commonly observed in most flames. The local soot parameters in the flame, which would be of interest, are soot loadings, agglomerate number densities, agglomerate diameters, spherule diameters and, thus, degrees of agglomeration.

Prado *et al.* (1981) have investigated the effect of temperature on the process of soot formation in a propane–air premixed flame [see also Prado and Lahaye (1981)]. They found that for a given fuel air ratio the local soot volume fraction decreases throughout the flame with increasing temperature. At the same time the soot agglomerate diameter decreases with increasing temperature as do the spherule diameters. This is in accordance with the reduction of the sooting tendency of premixed flames with increasing temperature reported by Glassman (1979).

On the other end of the spectrum, earlier work by Lahaye and Prado (1978) and Prado and Lahaye (1981) on the oxygen-free pyrolysis of methane and benzene indicates that in such a system the amount of soot formed increases with temperature. Spherule diameters decreased slightly with increasing temperature, and agglomerate dimensions were not measured. An increase with temperature in the sooting tendency of benzene during pyrolysis was also observed by Vaughn *et al.* (1981) during shock tube studies up to a temperature of about 2000°K.

Most diffusion flames may be considered to consist of a largely oxygen-free pyrolysis region surrounded by a flame front. It is the purpose of this study to determine the local soot concentrations and soot particle properties within such a flame.

II EXPERIMENTAL APPARATUS AND PROCEDURE

Burner

A Parker Wolfhard burner which supports two vertical flat flame sheets was chosen for this study in order to avoid the need for a deconvolution of the absorption signal necessary in flames of cylindrical geometry [see Jagoda *et al.* (1980) and Santoro *et al.* (1983)]. The burner, which is similar to the one used by Kent *et al.* (1981) and Haynes and Wagner (1980), consists of three parallel slots 51 mm in length. The outer slots, which carry the oxidizer, have a width of 16 mm each, while the inner fuel slot is 5 mm wide. For equal fuel and oxidizer burner exit velocities this results in a stable, somewhat underventilated flame. The burner is surrounded by a nitrogen-carrying jacket to exclude drafts and to prevent end-flamelets from forming across the width of the fuel slot. Further flame stabilization is assured by the use of screens near the tip of the flame. In order to permit steady operation over extended periods of time the burner housing is water cooled. The burner can be displaced in the vertical and horizontal directions to enable measurements to be carried out in different parts of the flame without disturbing the optical system.

Diagnostics

A simultaneous laser light scattering and absorption system similar to the one pioneered by D'Alessio *et al.* (1975) and described in detail by Jagoda *et al.* (1980) has been set up. The beam from a 4-Watt argon ion laser operating at 514.5 nm is focused into the test section in the flame using a 30 cm focal length lens and passes along the flat flame sheet onto a photomultiplier which measures the intensity of the transmitted light. A second photomultiplier is used to monitor the intensity of the beam scattered at 90° to the incident beam. A system of lenses and apertures limits the solid angle over which scattered light is collected and eliminates radiation from any part of the laser beam other than the $60 \times 60 \times 100$ micron test volume under consideration. Direct radiation from the flame to the photomultiplier is reduced using a monochromator and a narrow band width interference filter. The remaining stray light is eliminated by placing a chopper in the incident beam and passing the output from the photomultiplier through a phase sensitive detector which amplifies only the signal in constant phase with the chopper, *i.e.*, radiation originating from the laser beam. The absorption and scattering signals are observed on an oscilloscope and registered on a chart recorder.

The Mie Theory in the Rayleigh approximation as detailed by Kerker (1969) is used to obtain the local soot volume fractions, F_v, the mean soot aggregate diameters, D, and number densities, N, of the soot agglomerates from the absorption and scattering measurements.

The scattering cross sections, C_{sca}, of the soot aggregates were determined from the measurement of the incident and scattered intensities of the laser beam, while the extinction coefficients, K_{ext}, were found from the incident and transmitted intensities (Beer–Lambert law). The mean scatterer diameters and their number densities were obtained from their scattering cross-sections and extinction coefficients, while the extinction coefficients by themselves yielded the soot volume fractions. The details of the mathematical relationships used have been derived from Kerker (1969) and are listed by D'Alessio *et al.* (1975), Haynes and Wagner (1980), Kent and Wagner (1982),

Santoro *et al.* (1983) and others. They will, therefore, not be repeated here. It is interesting to note that the determination of K_{ext} is less precise than that of C_{sca} since the absorption measurements integrate over the entire length of the flame and are, therefore, dependent on its two-dimensionality. Small deviations from perfect flame flatness and the possible existence of small end-flames reduce the accuracy in the determination of K_{ext}. Since N is proportional to the square of K_{ext}, their values may be expected to be less accurate than those of D which only varies as the inverse of the cube root of K_{ext}.

The determination of C_{sca} from the measurements of scattered intensity depends on a number of geometric parameters of the scattering system. Rather than measure these parameters, the system was calibrated with pure nitrogen and methane whose scattering cross-sections were calculated using expressions taken from Penney (1969) and Müller–Dethlefs (1979). The calculated scattering cross-sections of the calibration gases compared very well with these quoted by Rudder and Bach (1968) for the respective wavelengths. This technique has previously been used by D'Alessio *et al.* (1975) and Jagoda *et al.* (1980).

A monodisperse distribution of spherical soot particles was assumed. Therefore, when comparing the results presented in the next section with those obtained by Santoro *et al.* (1983), who assumed self-preserving or log normal distributions, the diameters determined here correspond to their $D_{6,3}$, while the number density must be multiplied by 2. Since in Santoro's treatment the soot volume fraction is given by $ND_{3,0}^3$ and the ratio $(D_{6,3}/D_{3,0})^3=2$, the soot volume fraction is unchanged.

The Mie theory of scattering in the Rayleigh approximation assumes spherical scatterers whose $D \ll \lambda$. This latter criterion is not strictly observed, but it can be shown that for particles of 100 nm diameter the error introduced is only of the order of 10 percent. Furthermore, the soot aggregates are not spherical and only "equivalent diameters" could, therefore, be established.

Both scattering and extinction measurements had to be averaged over excursions of the order of 5 percent in most parts of the flame. In areas of steep soot concentration gradients, these fluctuations due to small movements of the flame were somewhat bigger, but the results were, nevertheless, reproducible.

The optical measurements described above are a function of the properties of the agglomerates. The spherules which make up the agglomerates cannot be detected in this way. Soot was, therefore, extracted from various locations in the flame to determine the spherule diameter distributions using transmission electron microscopy. The effect of this procedure on the flame had previously been checked and found to be small (Jagoda *et al.*, 1980). Local degrees of agglomeration could, thus, be obtained by comparing the agglomerate dimension obtained from the optical measurements with the spherule diameters measured on the electron micrograph. When viewing the electron micrographs, extensive agglomeration can also be observed. This, however, is due mostly to agglomeration during sample collection and treatment, and is not representative of the degree of agglomeration in the flame. The diameters of the spherules, on the other hand, may be expected not to change because of the rapid quenching of the chemical reactions in the probe. It is, therefore, important to realize that the scattering and microscopy techniques are truly complementary.

The temperature distribution in the flame was measured using uncoated Pt, Pt–13% Rh thermocouples with a 125 micron diameter junction. Conductive losses were minimized by introducing the leads parallel to the flame sheet. Since relative temperatures rather than their absolute values are of interest here, the thermocouple results were not corrected for radiative losses.

Flame Temperature Variation in a Diffusion Flame

In this study the effect of temperature on the sooting process in a propane–air diffusion flame has been investigated. In the flame front of a diffusion flame the combustion proceeds, essentially, under stoichiometric conditions. For given fuel and oxidant compositions the adiabatic flame temperature is, therefore, essentially fixed. In order to be able to introduce a variation in adiabatic flame temperature for the diffusion flames, the inert nitrogen content of the oxidizer, which acts as a diluent, was varied. A decrease in nitrogen content, thus, corresponds to an increase in flame temperature, and vice versa. Results for flames of oxygen to nitrogen ratios, by mole, in the oxidizer flow of 0.27, 0.33 and 0.41 will be reported here. These flames will be referred to as "a", "b" and "c". Adiabatic flame temperatures T_{ad}, were calculated for these three cases taking into account the equilibrium concentration within the flame as computed using the NASA code developed by Gordon and McBride (1971).

III RESULTS AND DISCUSSION

Soot volume fractions, soot aggregate diameters and their number densities for flames of three adiabatic flame temperatures are reported here. They correspond to oxygen to nitrogen ratios of 0.27, 0.33 and 0.41 with calculated adiabatic flame temperatures of 2279, 2417 and 2540°K. The fuel was pure propane, and the cold gas velocity of fuel and oxidizer was maintained at 6 cm/sec for all cases.

Figure 1 shows the temperature distribution in the vertical plane normal to the burner slots for flame "a". It is observed that the flame front temperature remains constant with height in the part of the flame investigated. As one moves horizontally away from the flame front the temperature drops both in the direction towards the fuel and the oxidizer. In the pyrolysis zone, near the center, the temperature increases somewhat with height.

The temperatures in the flame fronts for the flames with higher oxygen to nitrogen ratios (*i.e.*, "b" and "c") were found to be above the melting point of platinum, causing the thermocouples to break. In order to obtain an indication of the relative temperature changes between the three flames, a shielded Pt, Pt–13% Rh thermocouple was used at selected positions in all three flames. This probe resulted in lower readings because of the heat loss due to the shield and no melting occurred. It was noted that the ratios between measured "shielded" temperatures in the flame front and calculated adiabatic flame temperatures were the same for all three flames within 1 percent. Flame temperatures for flames "b" and "c" were, therefore, extrapolated by multiplying the ratio between the unshielded measured temperature of flame "a" and its calculated adiabatic flame temperature by the calculated adiabatic flame temperatures for flames "b" and "c". Values for the flame front temperatures of 1973°K for flame "a", 2063°K for flame "b" and 2195°K for flame "c" were, thus, obtained. The shapes of the isotherm lines for the three flames are assumed to be similar.

The distributions of soot volume fraction versus distance from the burner center for different heights above the flame for the three flames are shown in Figure 2a, b and c. For all three flame temperatures the entire sooting region lies well within the fuel side of the flame and its soot content increases with height above the burner. The amount of soot produced at any given height above the burner increases with increasing flame temperature. Furthermore, comparison between Figures 2a, b and c shows that the increase in temperature leads to soot being formed earlier in the flame. Thus, the

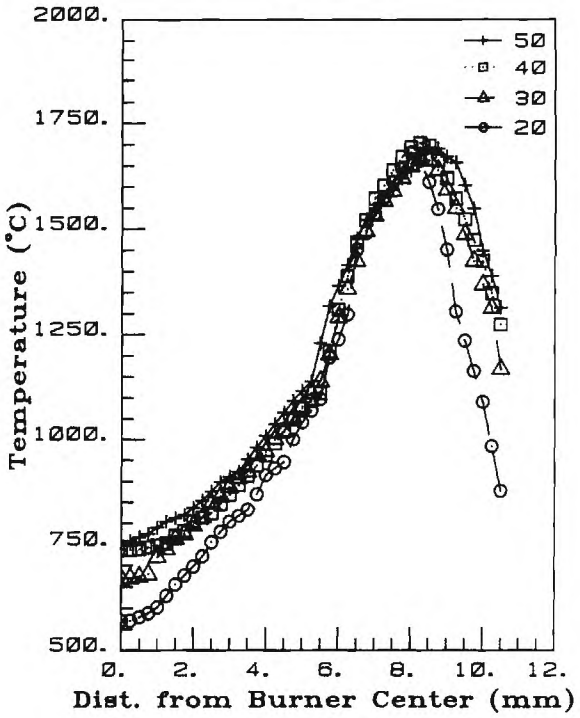

FIGURE 1 Temperatures versus distance from burner center at different heights above the burner for the flame with $T_{ad}=2279°K$.

increase in temperature accelerates the production of soot precursors and pyrolysis products for soot growth in the lower region of the flame prior to soot formation. This occurs even though oxygen may be entrained into the pyrolysis zone due to quenching near the burner mouth which causes the anchor region of the flame to be more premixed in nature. In the upper part of the flame the increase in temperature results in an increase in pyrolysis rate, as postulated by Glassman *et al.* (1981). This leads to the observed increase in soot loadings and, therefore, to the increase in sooting tendency with temperature which they observed in diffusion flames.

In Figure 3 the mean soot aggregate diameters are plotted against distance from the burner center for different constant heights above the burner for the three different flames. For all cases the regions of maximum soot mass loading also correspond to those in which soot agglomerates of largest diameters are found. Clearly the mean soot aggregate diameters increase with increasing height in the flame for all temperatures investigated. Furthermore, the increase in temperature has the effect of increasing the soot agglomerate sizes found at given heights above the burner.

The aggregate number density distributions shown in Figure 4, on the other hand, follow a different trend. For all flames the maximum number of particles exists closest to the flame front. While more particles seem to be present near the flame front in the lower part of the flame than in the upper part, their number density decreases towards a common level in the region of maximum diameters and soot

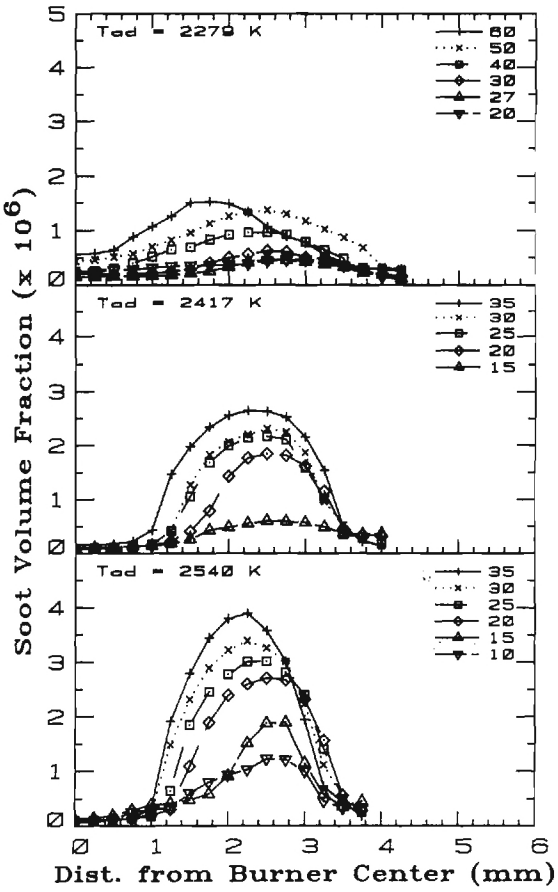

FIGURE 2 Soot volume fractions versus distance from burner center at different heights above the burner for three adiabatic flame temperatures.

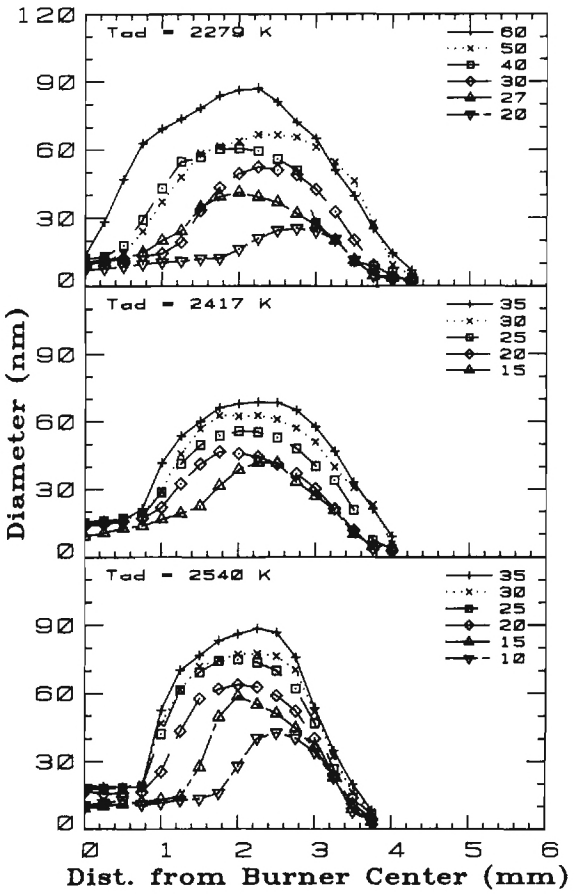

FIGURE 3 Soot agglomerate diameters versus distance from burner center at different heights above the burner for three adiabatic flame temperatures.

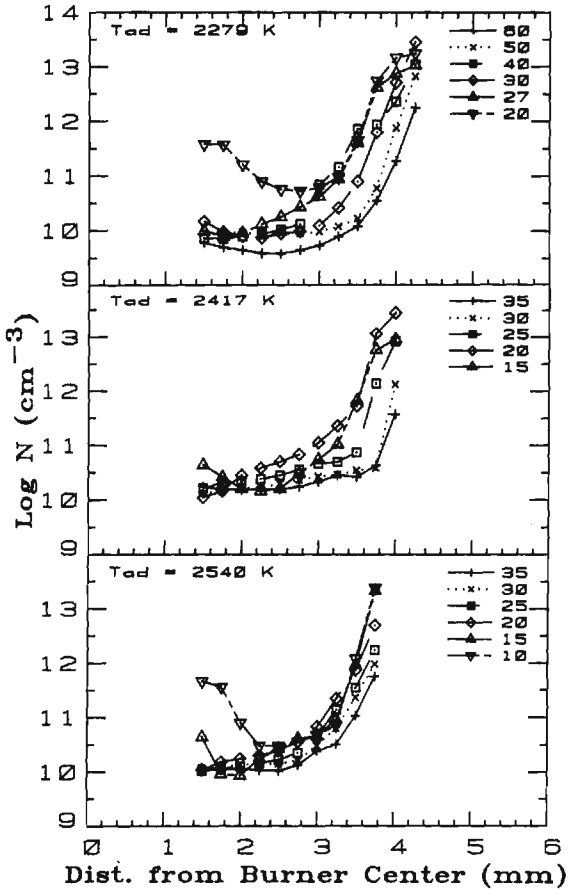

FIGURE 4 Soot agglomerate number densities versus distance from burner center at different heights above the burner for three adiabatic flame temperatures.

concentration. As mentioned in the previous section, the values of number densities are less reliable than those obtained for mean diameters and soot volume fraction because of their strong dependence on K_{ext}. Since the absorption near the burner center was relatively small and was influenced by the possible existence of end-flames and large polycylic aromatic hydrocarbons in the fuel rich part of the flame, number densities are only plotted up to 1.5 mm from the burner center. For similar reasons the soot volume fractions and diameters near the burner center plotted in Figures 2 and 3 may be somewhat high. Careful inspection of Figure 3a indicates that there is a detectable decrease in the number density of soot particles with height above the burner suggesting an agglomeration in excess of the possible creation of new particles. Bearing in mind the reduced accuracy in the number density determination, it appears that there is little change in the number density with increasing flame temperature, except a somewhat smaller number of particles near the upper part of the flame front at higher temperatures.

The increase in soot volume fractions with temperature, therefore, appears to be due to an equal number of larger soot agglomerates being present in the hotter flames. Whether the increase in diameters of the mean soot agglomerates is due to an increase in the diameters of the fundamental spheroids which make up these agglomerates or to more extensive agglomeration could not be determined from the optical measurements. Soot samples were, therefore, extracted at heights above the burner at which the aggregate properties had been determined for the three flames. Unfortunately, the spatial resolution for sampling is not as good as that for the optical measurements, and only an average sample per height could be obtained. These samples were viewed under a transmission electron microscope and the diameter distributions of the soot spheroids were recorded. The mean spherule diameters are plotted versus height above the burner in Figure 5. The diameter of these elementary soot particles increases

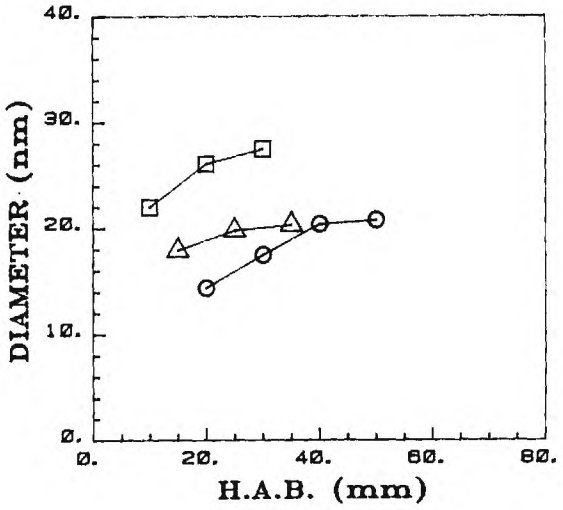

FIGURE 5 Mean spherule diameters versus height above burner for three adiabatic flame temperatures.

with height in the flame due to surface growth, for all three flame temperatures. This growth is particularly pronounced in the early part of the flame. Flames of higher temperature cause the formation of somewhat larger spherules. In particular, the soot spheroids found in the flame "c" are about 50 percent larger than those in the other two flames.

Since the agglomerates, unlike the spherules, are not spherical, their measured diameters correspond to "equivalent diameters". Their degree of agglomeration was estimated by comparing the mean volume of the spherules with that calculated using the equivalent diameter of the agglomerates as determined by the light scattering method. These degrees of agglomeration were determined using the largest mean agglomerate diameters observed at the different heights in each of the three flames. Table I indicates that the degree of agglomeration increases with distance in the flame for all three flames. The general trend in Table I suggests that, overall, the agglomeration process is accelerated by the increase in flame temperature from flame "a" to flame "b" but is slightly lower for the much larger soot spheroids present in flame "c" within the experimental accuracy.

TABLE I

Mean degree of agglomeration for flames "a", "b" and "c"

Ht. ab. Burner/adiab. fl. temp. (°K): (mm)	2279	2417	2540
10	—	—	7.3
15	—	12.9	—
20	5.6	—	14.7
25	—	22.3	—
30	27.1	—	22.6
35	—	38.6	—
40	26.1	—	—
50	33.4	—	—

The optical results described above are in good agreement with measurements carried out in flames using a different fuel by Kent *et al.* (1980) and by Haynes and Wagner (1980), as well as by Santoro *et al.* (1983) using a cylindrical burner. A leveling off of soot volume fraction in the upper part of the flame observed by Kent *et al.* (1980) was observed only in flame "a". Measurements in flame "b" and "c" were not carried out sufficiently close to their flame tips. Sampling to obtain spherule dimensions and, thus, degrees of agglomeration were not carried out by these workers. Nor did they investigate the effect of temperature on the individual soot parameters.

The overall steps in the formation of soot in diffusion flames as detailed by Haynes and Wagner (1980) appear to be valid for all flame temperatures investigated here. They are very briefly summarized for completeness and reconfirmed in light of the additional spheroid measurements reported here. For all flame temperatures the great majority of soot particles are created in the high temperature region near the flame front where the particle density is high but their diameters are small. This rate of nucleation seems to decrease somewhat with height above the burner especially for higher flame temperatures. As these particles move upward by convection as well as

away from the flame front towards the burner center by convection and thermophoresis, they grow by agglomeration as witnessed by the decrease in number density away from the flame front and their increase in degree of agglomeration with height above the burner. Agglomeration by itself, however, does not lead to an increase in soot volume fraction. This increase of soot loading must, therefore, be ascribed to surface growth as also indicated by the increase in spherule diameter in the downstream direction. The rate of surface growth has been shown to increase with flame temperature. This increase in the rate of soot formation due to surface reactions is likely to be due not only to an increase in gaseous species available for adsorption at the higher temperatures, but also to the larger surface areas presented by the larger spheroids. Some particles may also be formed as one moves towards the region of high soot concentration, but this generation rate must be small since the particle number decreases and the mean diameter increases in this direction indicating that aggregation predominates. This aggregation process is most pronounced in the vicinity of particle inception, *i.e.*, the number of particles decreases most sharply near the flame front. This may be due to the higher number densities leading to more frequent collisions in these regions, but it also indicates a greater tendency of the small, reactive "young" soot particles to stick together because of the presence of free radicals adsorbed on their surfaces. The process of aggregation, however, continues to some extent farther from the flame front as shown by the increase in degree of agglomeration with height above burner measured for all flames investigated. While an increase in temperature does not result in a noticeable change in aggregate number densities in the areas of appreciable soot loadings in the flame, more nuclei, which are not readily detectable, may be formed near the flame front of the hotter flames. An increased coagulation rate along with heavy surface growth in that region would then be responsible for the lack of change in aggregate number densities observed in the region where measurements can be made, while contributing to the larger spheroids and agglomerates found in the hotter flames. The smaller particles observed near the center of the flames may have been formed in the early part of the flame and have spent less time in the region of growth as suggested by Haynes and Wagner (1980).

In order to quantify the effect of the flame temperature on the global reaction rate of the soot formation reaction, the total soot volume fraction at different heights above the burner (*i.e.*, area under soot volume fraction plots) and the corresponding maximum aggregate diameters were plotted versus residence time. The residence time is defined as the time required for a pocket of gas to travel from the burner to a given height. This is not to suggest that all soot particles are formed near the burner mouth and grow as they move in a vertical direction through the flame. On the contrary, it has been shown that new particles are continuously being formed near the flame front at all heights. Since, however, the total soot loading at any given height in the flame is a result of the cumulative formation of soot up to that point, a fair comparison of the soot formation rates for different temperatures can only be obtained by comparing soot loadings in the flame for equal gas residence times. This takes into account any changes in vertical velocities due to the changes in temperature. Changes in thermophoresic velocity were neglected since these are only significant in the horizontal direction. A similar normalization was carried out for soot aggregates of maximum diameter at each height in the flame since the largest aggregates may be expected to, generally, result from soot spherules first formed in the early part of the flame.

Since no velocity measurements were carried out in this flame, the residence time in the flame had to be related to the height above the burner using theoretical considerations. Kent and Wagner (1980), who carried out velocity measurements in a

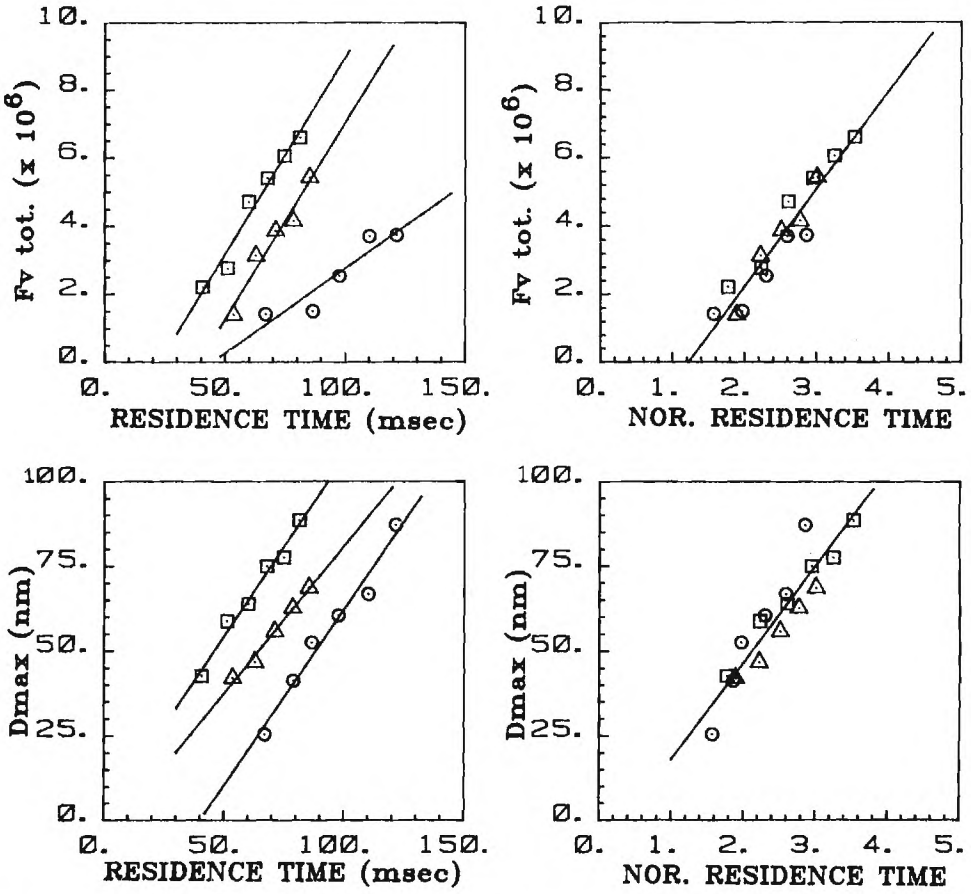

FIGURE 6 Total soot volume fractions at different heights above burner versus residence time (a), and normalized residence time (b); maximum soot agglomerate diameters at different heights above burner versus residence time (c), and normalized residence time (d).

similar diffusion flame, have established that buoyancy forces cause considerable acceleration of the vertical velocities in this type of flame. The relationship between the time required to reach a given vertical position and its height above the burner is, therefore, not linear.

A simple, one-dimensional model of two parallel streams of gases of differing densities based on the work by Powell and Browne (1956) was, therefore, developed. This model takes into account both the difference in density of fuel and oxidizer and the difference in temperature of the combustion products and the surrounding oxidizer flow. The details of this model are presented in the Appendix. Using the fuel and flame temperatures reported by Kent and Wagner (1980), their measured fuel velocities could be predicted with good accuracy, particularly by fitting the density ratio mentioned in the Appendix using the velocity measured at one point 90 mm above the

burner. This model was applied to the flames presented here and their vertical velocities were predicted from the temperature distribution measured. These vertical velocity distributions were used to convert the 'height above the burner" into a time axis.

Figure 6a shows the variation of total soot volume fraction at given heights with residence time in the flame for all three flame temperatures. The increase in soot mass loading with temperature is clearly seen, while there seems to be a pronounced increase in soot formation rate (slope) in going from flame "a" to flames "b" and "c". The observed, less steep slope for flame "a" may, however, partly be caused by a leveling off in soot formation rate in the upper part of that flame.

A plot of maximum agglomerate diameter versus residence time (Figure 6c) shows that the rate of agglomerate growth (slope) is almost independent of temperature. The absolute values of the soot agglomerate diameters, however, are larger for higher flame temperatures. This increase with temperature is due, partially, to increased spherule diameters (Figure 5) and, partially, to increased agglomeration (Table I).

In order to normalize the data in Figures 6a and 6c and to obtain an "effective" growth residence time", which includes the effect of temperature on the sooting rate, the residence time for every height above the burner in each flame was divided by its residence time to the first measured appearance of soot. This was considered permissible, in spite of the difference in activation energy and, thus, the sensitivity to temperature of the nucleation and surface growth reactions, since both nucleation and considerable surface growth have taken place prior to the first experimental detection of soot at the base of the flame. Furthermore, nucleation continues at all heights above the burner, so that both nucleation and growth have taken place in each residence time interval over which soot measurements were carried out.

When total soot volume fractions are plotted against those normalized residence times, the points do, indeed, fall close to a single line as shown in Figure 6b. Similarly, Figure 6d shows an almost linear dependence of maximum diameters against normalized residence time.

IV CONCLUSIONS

The *in situ* soot parameters including soot loading, soot aggregate diameters and number densities, as well as spherule diameters have been determined for propane diffusion flames at three different flame temperatures. The general features of the distributions of these parameters are similar for all three cases and agree well with the observations made by other workers studying diffusing flames of different fuels at a single flame temperature. In addition soot spherule sizes and degrees of agglomeration were seen to increase with height above the burner for all flames studied.

As the flame temperature is increased, soot is beginning to be formed earlier in the flame. At the same time the soot loading at given heights above the burner increases. This more extensive sooting at higher temperature was found to be due to larger soot agglomerates which, in turn, are formed partially by an increase in the size of the spherules and partially by an increase in the degree of agglomeration. The agglomerate number densities are largely insensitive to the change in the flame temperature, although the number of incipient spheroids near the flame front, which are too small to measure, may have been affected. Even though buoyancy causes considerable acceleration of the flame gases in the vertical direction, the difference in temperatures

between the three flames is sufficiently small to affect the gas residence times in the flames by only a small amount (<7 percent). All observations detailed above are, thus, still valid even when considering soot loading and particle diameters as a function of gas residence time in the flame rather than heights above the burner. The rates of growth of the maximum soot agglomerate diameters, as determined from the slopes of the curves of these diameters plotted against non-normalized residence time, appear largely insensitive to temperature. The absolute values of these maximum diameters, however, increase with flame temperature which accounts for the larger soot volume fractions observed in the hotter flames.

Lastly, it was shown that an "effective growth residence time" may be defined such that both total soot volume fraction and maximum soot diameters vary linearly with that normalized time for all flame temperatures. This is, of course, not to say that the rate of soot formation does not vary with temperature but rather that the effect of temperature may be included in the normalization. In conclusion, it is felt that the findings reported here help to shed new light on the global observation by Glassman (1979) and others, which have reported an increase of sooting tendency with temperature for diffusion flames.

ACKNOWLEDGEMENT

The authors wish to thank the U.S. Environmental Protection Agency and the monitor, Mr. D. F. Carey for their support. Although the information described in this article has been funded wholly or in part by the United States Environmental Protection Agency under assistance agreement No. R-808953-02-0 to the Georgia Tech Research Institute, it has not been subjected to the Agency's required peer and administrative review and, therefore, does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Appendix

CORRECTION FOR BUOYANCY

The model used to correct the velocity field in the flame for the effect of buoyancy is based on an analysis by Powell and Browne (1956) which deals with the investigation of the effect of the differing densities of cold fuel and oxidizer streams upon the fluid dynamic characteristics of diffusion flames. This model was expanded to take into account the effect of the differing temperatures of the combustion gases and the oxidizer stream upon their densities. The fuel at temperature T_f and oxidizer at temperature T_o are assumed to leave the burner in parallel streams with velocity u_i at height $y=0$. The cross-sectional area of the oxidizer and fuel streams at $y=0$ are A_{o_i} and A_{f_i} respectively. The streams are bounded on the outside by parallel walls, but the position of the interface between the two streams (which corresponds to the reaction zone) is free to vary with height such that the cross-sectional areas of the two streams also vary with height with $A_f+A_o=A=$constant. Frictional effects at the walls and the interface are neglected, and at each height the pressures in the two streams are equal. It is also assumed that T_o and T_f do not vary with height.

Applying Bernoulli's equation to each stream separately between stations o and y and using $P_f = P_o$ yields:

$$(u_o/u_i)^2 - (\rho_f/\rho_o)(u_f/u_i)^2 = \left[\frac{Y}{(u_i^2/2g)}\right][(\rho_f/\rho_o) - 1] \tag{A-1}$$

Conservation of mass for the two streams gives:

$$u_o/u_i = \frac{(u_f/u_i)}{(1+r)(u_f/u_i) - r} \tag{A-2}$$

where the area ratio $r = A_{f_i}/A_{o_i}$. The density ratio ρ_f/ρ_o is given by

$$\rho_f/\rho_o = (m_f/m_o)(T_o/T_f) \tag{A-3}$$

where m_f and m_o are the molecular weights of the fuel and oxidizer and the temperatures are absolute.

Equations (A-1) and (A-2) must be solved simultaneously in order to obtain the fuel and oxidizer velocities, u_f and u_o, as functions of height above the burner, y. The parameters that must be specified are the fuel/oxidizer area ratio, r, the initial velocity u_i, and the fuel and oxidizer temperatures, T_f and T_o. These latter values must be obtained from temperature measurements in the flame, and are needed to obtain the density ratio ρ_f/ρ_o. In solving these equations, it is convenient to use the dimensionless variables $U_f = u_f/u_i$, $U_o = u_o/u_i$ and $Y = y/(u_i^2/2g)$. A computer code was developed to solve equations (A-1) and (A-2) numerically by an iterative technique.

In order to evaluate the model, velocities were calculated for the ethylene/air flames investigated by Kent *et al.* (1981). For their burner $r = 0.05$ and $u_i = 7$ cm/sec. The temperatures T_o and T_f were estimated from the measured temperature profiles they presented for various heights. Thus T_f was taken to be 1300°K. The oxidizer temperature was more difficult to estimate so two cases were considered: (1) $T_o = 300$°K (room temperature) and (2) $T_o = 800$°K (mean between room temperature and T_f). The model predicts excessive vertical fuel velocities for $T_o = 300$°K ($\rho_f/\rho_o = 0.221$) and deficient fuel velocities for $T_o = 800$°K ($\rho_f/\rho_o = 0.615$). A curve fit was also obtained by matching the experimental data at 90 mm by choosing $\rho_f/\rho_o = 0.368$. This gives excellent agreement with the experimental data down to 30 mm. The small deviations of the experimental data from the theoretical curve for heights below 30 mm are most likely caused by vertical temperature gradients in the flame. This model was used to calculate the vertical velocity distribution in the flame which, in turn, was used to convert "heights above the burner" to time elapsed from the instant a pocket of gas leaves the burner mouth. These calculations showed that while the gas velocity in the flame is strongly affected by buoyancy (6 cm/sec at the burner mouth to 85 cm/sec at 5 cm above the burner for flame "a") the difference in residence time to reach a given height for the 3 flames is small (*e.g.*, 83.6 msec in flame "a", 78.5 msec in flame "b" and 74.8 msec in flame "c" to reach a height of 30 mm above the burner). The increase of soot content and soot aggregate diameter with increasing temperature is, thus, valid even when considering the data as a function of "time elapsed" rather than "height above burner".

REFERENCES

Calcote, H. F. (1981). Mechanism of soot nucleation in flames—A critical review. *Comb. Flame* **42,** 215.

D'Alessio, A., DiLorenzo, A., Micera, G., and Beretta, F. (1975). Laser light scattering measurements in the soot nucleation zone of rich methane–oxygen flames. *2⁰ Simposio di Dinamica della Reazioni Chimiche*, Padova, pp. 147–156.

Dalzell, W. H, and Sarofim, A. F. (1969). Optical constants of soot and their application to heat flux calculations. Trans. ASME, *J. Heat Transf.* **91,** 100.

Dearden, P., and Long, R. (1968). Soot formation in ethylene and propane diffusion flames. *J. Appl. Chem.* **18,** 243.

Glassman, I. (1979). Phenomenological models of soot formation in combustion systems. Princeton University Mech. and Aero Eng. Rep. No. 1450.

Glassman, I., and Yaccarino, P. (1980). The effect of oxygen concentration on sooting diffusion flames. *Comb. Sci. and Tech.* **24,** 107.

Glassman, I., and Yaccarino, P. (1981). The temperature effect in sooting diffusion flames. *Eighteenth Symposium (International) on Combustion*, Waterloo, pp. 1175–1183.

Haynes, B. S., and Wagner, H. G. (1980). Sooting structure in a laminar diffusion flame. *Ber. Bunsenges. Phys. Chem.* **84,** 499.

Haynes, B. S., and Wagner, H. G. (1981). Soot formation. *Prog. Energy Combust. Sci.* **7,** 229.

Holve, F. J. (1974). Diffusion controlled combustion of polymers. Ph.D. Thesis, Department of Mechanical Engineering, University of California, Berkley, Report ME-74-4, Chap. 4.6.2, pp. 68–76.

Homan, K. H. (1967). Soot formation in premixed flames. *Comb. Flame*, **11,** 265.

Howard, J. B., and Kausch Jr., W. J. (1980). Soot control by fuel additives. *Prog. Energy Combust. Sci.* **6,** 263.

Jagoda, J. I., Prado, G., and Lahaye, J. (1980). An experimental investigation into soot formation and distribution in polymer diffusion flames. *Comb. Flame* **37,** 261.

Kent, J. H. (1970). A noncatalytic coating for platinum–rhodium thermocouples. *Comb. Flame* **14,** 279.

Kent, J. H., Jander, H., and Wagner, H. G. (1981). Soot formation in a laminar diffusion flame. *Eighteenth Symposium (International) on Combustion*, Waterloo, pp. 1117–1126.

Kent, J. H., and Wagner, H. G. (1982). Soot measurements in laminar ethylene diffusion flames. *Comb. Flame* **47,** 53.

Kerker, M. (1969). *The Scattering of Light and other Electromagnetic Radiation.* Academic Press, New York and London, Chap. 3.2, pp. 31–39.

Lahaye, J., and Prado, G. (1978). Mechanisms of carbon black formation, in Walker, P. L. and Thrower, P. A. (Eds.), *Chemistry and Physics of Carbon*, Marcell Dekker, New York, Vol. 14, pp. 168–294.

Müller-Dethlefs, K. (1979). Optical studies of soot formation and the addition of organic peroxides to flames. Ph.D. Thesis, Imperial College, University of London, Chap. 3, pp. 23–38.

Neville, A. E. (1972). America burning. Report of the National Commission on Fire Prevention and Control. Chap. 9, pp. 61–69.

Palmer, H. B., and Cullis, C. F. (1965). The formation of carbon from gases, in Walker, P. L. (Ed.), *Chemistry and Physics of Carbon*, Marcell Dekker, New York, Vol. 1, pp. 265–325.

Penney, C. M. (1969). Light scattering in terms of oscillator strengths and refractive indices. *J. Opt. Soc. Am.* **59,** 34.

Powell, E. A., Bankston, C. P., Cassanova, R. A., and Zinn, B. T. (1979). The effect of environmental temperature upon the physical characteristics of the smoke produced by burning wood and PVC samples. *Fire and Materials* **3**(1), 15.

Powell, H. N., and Browne, W. G. (1956). Some fluid dynamic aspects of laminar diffusion flames. *Sixth Symposium (International) on Combustion*, New Haven CT, pp. 918–922.

Prado, G., and Lahaye, J. (1981). Physical aspects of nucleation and growth of soot particles, in Siegla, D. C. and Smith, G. W. (Eds.), *Particulate Carbon Formation During Combustion*, Plenum Press, New York–London, pp. 143–176.

Prado, G., Jagoda, J. I., Neoh, K., and Lahaye, J. (1981). A study of soot formation in premixed propane/oxygen flames by *in-situ* optical techniques and sampling probes. *Eighteenth Symposium (International) on Combustion*, Waterloo, pp. 1127–1136.

Rudder, R. R., and Bach, D. R. (1968). Rayleigh scattering of ruby-laser light by neutral gases. *J. Opt. Soc. Am.* **58**(9), 1260.

Santoro, R. J., Semerjian, H. G., and Dobbins, R. A. (1983). Soot particle measurements in diffusion flames. *Comb. Flame* **51,** 203.

Schug, K. P., Manheimer-Timnat, Y., Yaccarino, P., and Glassman, I. (1980). Sooting behavior of gaseous hydrocarbon diffusion flames and the influence of additives. *Comb. Sci. and Tech.* **22,** 235.

Vaughn, S. N., Lester, T. W., and Merklin, J. F. (1981). A single pulse shock tube study of soot formation from benzene pyrolysis, in Treanor, C. E. and Hall, J. G. (Eds.), *Shock Tubes and Waves, Proc. Thirteenth Symposium on Shock Tubes and Waves,* Niagara Falls, State University of New York Press, Albany, NY, pp. 860–868.

Wagner, H. G. (1981). Soot formation in combustion. *Eighteenth Symposium (International) on Combustion,* Waterloo, pp. 3–19 (Plenary Lecture).

December 12, 1984

Mr. Donald F. Carey
Science Review Administrator (RD-675)
Environmental Protection Agency
Washington DC 20460

Dear Mr. Carey:

Enclosed please find a draft of our proposed final report. As we discussed, the report consists of the two refereed papers resulting from this work which have been accepted for publication and are presently in print and one Ph.D thesis. The most important findings are summarized in the attached Executive Summary. One further paper dealing with soot burn out is still under preparation.

Please let us know whether the enclosed format is acceptable or what changes need to be made. Please also let us know how many copies each are required of the Executive Summary, the papers and the thesis. We appologize for the delay in sending you this report but the student has only just completed his thesis.

I want to take this opportunity to thank you again for giving us the opportunity to carry out this work and hope that we will be able to work for you again in the not too distant future.

Yours sincerely,

J. Jagoda
Asst. Professor

JJ/jj

Encl:

Soot Formation in Gaseous Diffusion Flames

Final Report

Submitted to the

United States Environmental Protection Agency

Under Contract # R 80895 3010

By

J. I. Jagoda, Principal Investigator

School of Aerospace Engineering

Georgia Institute of Technology

December 1984

Executive Summary

The results obtained in this research project were reported in detail in the Ph.D Thesis submitted byMr. C. Wey to the School of Aerospace Engineering of the Georgia Institute of Technology (Ref. 1). Highlights were presented at the 1982 Fall Meeting of the Eastern Section of the Combustion Institute (Ref. 2), and published in two refereed publications (Ref. 3 & 4). One further presentation or publication is still under preparation. All these papers are included in the final report. The findings are, therefore, only summarized in this executive summary.

Soot formation in laminar diffusion flames was investigated under various conditions in flames on a Parker-Wolfhart burner. This particular configuration was selected since it results in a pair of flat flame sheets which makes it possible to carry out absorption measurements without the need for deconvolution as is required in cylindrically symmetrical flames.

Soot in diffusion flames is generally formed in five discrete steps which occur consequentially although they may occur simultaneous in some parts of the flame for different particles. The hydrocarbon fuel first decomposes pyrolytically and there recombines into large hydrocarbon molecules which are generally polyacetylens or polycyclic hydrocarbons. Some of these large hydrocarbons usually in the form of either radicals or ions act as soot precursors on which the soot particles nucleate. This nucleation process is thus the critical step in which liquid or solid hydrocarbons are first formed from the gaseous pyrolysis products. The

small particles or nuclei then grow by surface growth during which hycrocarbons are adsorbed on the surface to result in spherical particles or spheroids. Because the elementary particles are always spherical and since phase contrast electron microscopy has revealed a large number of almost graphite like layers of carbon atoms arranged in concentric shells about their respective nuclei, it is widely believed that the spherical particles pass through a liquid stage prior to their solidification pyrolysis about by dehydrogenation and cooling. A number of nucleation sites are generally observed in each soot spheroid which suggest that some agglomeration of partially solidified, small particles takes place in regions of strong surface growth resulting in larger, still spherical soot particles. This process is generally refereed to as coagulation and represent the fourth step in soot formation. Finally, the large spheroids agglomerate in zones of insufficient surface growth to result in spherical particles and the soot agglomerates are formed which are commonly observed in flame soot.

In order to be able to differenciate between the surface growth and coagulation steps which result in layer spherioids and the agglomeration process it was necessary to distinguish between soot spherules and their agglomerates. Two diagnostic techniques, in situ laser light scattering and absorption (LLSA) and suction probing followed by transmission electron microscopy (TEM) were therefore used to determine the physical properties of the soot generated in the diffusion flames.

Light scattered and absorbed from an incident beam by submicron sized particles depends on the intensity and wavelength of the incident light, the size of the scatterers and their number density. If these scatterers are agglomerates only their equivalent size and number density affects the scattering behavior. The LLSA method can, therefore, only be used to determine the physical properties of the agglomerates. To measure the spheroid diameters soot was extracted from various locations in the flames and viewed under TEM. This permitted the determination of the diameter distributions of the soot spheroids at different heights of the flame. Although extensive agglomeration may be observed in the TEM pictures most of this agglomeration occurred during sample collecting and treatment and is, therefore, not representative of the degree of agglomeration in the flame. LLSA and TEM measurements were, therefore, carried out in concert in order to obtain the properties of both the soot spheroids and their agglomerates. The details of the experimental set ups and procedures are described in the enclosed thesis and are, therefore, not repeated here.

Temperatures were measured throughout the different flames investigated using fine wire Pt-Pt 13% Rh thermocouples. Other techniques including sodium line reversal were also considered. It was, however, concluded that optical measurements of temperature could not be carried out in heavily sooting flames with the necessary spacial resolution. A possible exception is Coherent Antistokes Raman Spectroscopy (CARS) which, however, involves a capital outlay of approximately $300,000 for equipment not available in this department. Since soot is deposited on the

thermocouples a technique was developed which permitted the thermocouple to be moved back into the flame front to burn off the soot deposit between consecutive temperature measurements in the sooty zones of the flames. By monitoring the thermocouple output variations with time at each station it was possible to determine local temperatures with sufficient accuracy for the comparative studies in this project.

The following observations were generally made for all diffusion flames investigated and may, therefore, be considered as typical for diffusion flames. They are similar to results available from other workers for diffusion flames of different configurations, different fuels and under different conditions. Soot generally exist on the fuel side of the flame front as defined by the region of maximum temperature. As one moves from the flame front towards the center of the flame to the soot volume fraction and agglomerate diameters increase towards a maximum after which it drops off towards the flame center. Aggregate number densities, on the other hand, are highest near the flame front and drop off by as much as two orders of magnitude as one moves towards the flame center, where they level off.

In the downstream direction, both soot loadings and soot aggregate diameters increase with height in the flame. Higher up in the flame soot volume fraction maxima reach a limiting value and further soot loading leads to a spreading of the high soot concentration region towards the flame center until near the flame top the region of high soot loading reaches all the way to the flame center. Similarly a maximum aggregate diameter is

attained above which the particles do not grow. Soot aggregate number densities on the other hand do not change very much with height above the burner except for a slight decrease in number density near the base of the flame. Mean soot spherule diameters are seen to grow early in the flame and soon reach a maximum value. The results obtained in the immediate vicinity of the flame tip, where soot burn out occurs will be dealt with in detail later.

The above observations result in the following picture for the process of soot formation in a laminar diffusion flame. Nucleation takes place near the flame front where the particles are small and their number high. The small particles then move by convection and thermophoresis horizontally away from the flame front and vertically upward by convection. During this time the particles grow by coagulation and surface growth and eventually aggregate into agglomerates. The small particles found near the center in the lower part of the flame were formed very low near the flame front and spend only little time in the high temperature region where growth occurs. Higher up in the flame the region of higher temperature extends further towards the flame center and thus growth continues until larger particles are found throughout the flame. At the same time the region of heavy soot loading extends further and further towards the flame center similar to the behaviour of the combustion products in the classical Burke-Schuman flame. The exact reason for the limit on aggregate growth is not known, but similar observations were made in all flames investigated and were also reported by other workers.

Next the effect of the temperature on the individual steps leading to soot was investigated. The flame temperature was varied for these tests by varying the nitrogen diluent concentration in the oxidizer flow. Flame temperatures were measured and adiabatic flame temperature calculated. Previous investigations had shown that while an increase in flame temperature is premixed flames causes a reduction in soot, in diffusion flames sooting increases with temperature. These observations were made using global measurements such as sooting heights. These phenomena were explained in terms of competing oxidation and pyrolysis reactions. In a premixed flame the reaction rate of the oxidation is more sensitive to temperature than that of the pyrolysis resulting in less sooting. In diffusion flames no oxidation takes place in the pyrolysis flame and, therefore, an increase in temperature increases pyrolysis and thus sooting. In the present study the effects of temperature on the individual soot parameters were determined in situ. With increasing temperature, soot was seen to be formed earlier in the flame. Soot loadings for given heights above the flame were seen to increase with temperature as did the agglomerate diameters. Furthermore significant soot loading spread towards the flame front more rapidly. The maximum aggregate diameters also increased with higher flame temperatures. Soot spherules were seen to grow earlier and more rapidly and to reach a larger mean diameter. It was calculated that the large soot aggregate diameters are due to an increased agglomeration of somewhat larger soot spherules. Finally, it was shown that the increase in sooting with temperature could be normalized with respect to the height above the

burner at which soot was first observed. This does, indeed, suggest that pyrolysis is strongly affected by the temperature and that it is this which results in the increased sooting.

A number of previous investigations have shown that adding small quantities of oxygen to the fuel of a diffusion flame increases the flame's tendency to soot. Like in the case of early temperature effect investigations these observations were made using global soot measurements such as sooting height or total soot collected. A number of explanations were postulated for the increase in sooting upon the addition of oxygen to the fuel. In some papers the increase in temperature due to the extra oxygen is held responsible while other workers ascribe the increased sooting to the homogeneous catalytic action of the oxygen on the pyrolysis process. In this study the in situ sooting parameters were monitored as oxygen was added to the fuel of a diffusion flame in order to understand the mechanism by which oxygen addition to the fuel increases sooting.

Six flames with different oxygen concentration in the fuel ranging from zero to fifty percent were investigated. Fifty percent oxygen appears to represent a high oxygen concentration but it only corresponds to a fuel equivalence ratio of .1. All flames investigated behaved essentially as diffusion flames (as opposed to premixed flames) and their sooting patterns corresponded to those described for general diffusion flames in an earlier part of this report.

As the oxygen concentration in the fuel was increased, keeping total flow rates constant, a narrowing and considerable shortening of the flame use observed. Since this shortening was large compared to the change in equivalence ratio this may indeed be indicative of a catalytic action by the oxygen. As the oxygen content in the fuel was increased soot loadings and soot agglomerate diameters were seen to increase for given heights above the burner. Both local soot volume fractions and diameters tend to reach a maximum value after which increased soot loading is due to a spreading of the region of heavy soot loading towards the burner center. The most heavily oxigenated flames are actually too short to reach these limits and therefore, form somewhat less soot. This, however, is due to the shorter reaction time in these flames and not to a slower soot formation rate. When total soot loading is plotted versus time it is observed that the rate of soot formation increases with oxygen up to a concentration of 50% in the fuel of the diffusion flame. Only near the flame tip (which moves closer to the burner of more heavily oxygenated flames) is there a reduction in soot formation rate which eventually goes negative indicating burn out of soot. Addition of oxygen also causes a more rapid growth in the diameter of the soot aggregate. This diameter eventually decreases near the flame tip once soot burn out has commenced. The number density does not seem to be significantly affected by the oxygen addition. Soot spherule diameters, on the other hand do seem to increase somewhat once oxygen is added to the fuel. It is, therefore, apparent that the increased soot loading is caused by large aggregates which in turn are formed due to a somewhat increased agglomeration of slightly larger spherule particles. Some previous workers

had suggested that the global increase in sooting observed when one adds oxygen to the fuel of a diffusion flame is due to the resulting increase in flame temperature. From the relatively small temperature increases measured in these flames and the effect of the flame temperature on the soot formation process determined earlier in this work it can be stated that thermal effects cannot account for the large increase in sooting observed for these flames. Instead a chemical effect of the oxygen, probably in the form of a homogeneous catalysis seems to be indicated.

The amount of soot actually liberated from the flame is determined by a balance between soot generation and burn out. Therefore, and because of some interesting observations made during the earlier part of the work in the region near the flame tip, soot burn out was studied in perhaps slightly more detail than was suggested in the original proposal. This interest was indicated in the renewal proposal for the third year as well as in the recent request for a no-cost extension.

Since most of the soot burn out was expected to occur near the flame tip, a shorter flame was used for this part of the investigation. It was determined that the diffusion flame may be divided into three overall regions. In the lower part of the flame soot volume fractions, aggregate and spherule diameters increase because of the high rate of soot formation. Higher in the flame the convective component of velocity begins to carry the outer soot particles towards the flame front and further soot formation is accompanied by soot burn out. Close to the flame tip, soot burn out finally

dominates and soot volume fractions, aggregate and spherule diameters decrease with heights above the burner. From the distribution of the soot parameters near the flame tip it was determined that the small soot particle nearest the flame front burn out first. Early in the burn out region soot aggregate and spherule diameters both decrease indicating a burn out by surface oxidation. Closer to the tip, however, the decrease in spherule size slows while the reduction of the agglomerate sizes continues. Since, at the same time, the aggregate number density slightly increases, it seems to be possible that in the immediate vicinity of the flame front larger agglomerates split into smaller particles just prior to their burn out. A similar observation has recently been made during the burn out in lean premixed flames.

In summary, the effect of temperature and oxygen in the fuel of a propane air diffusion flame on the process of soot formation and the details of soot burn out in such flames were investigated. Details of the results were published in two refereed papers and a Ph.D thesis. One further paper is under preparation. All findings have, as far as possible, been tied in with previous observations and proposed theories of soot formation in the literature.

Two sets of measurements originally proposed could not be successfully carried out. The determination of localized ion concentrations in the sooty flame using a Langmuir probe proved difficult to carry out with the necessary spacial resolution. Furthermore butadiene could not be used as an alternate fuel since, during the lifetime of this assistance agreement,

OSHA declared butadiene a carcinogenic substance. Our laboratory is presently not equipped to handle toxic substances safely under combustion conditions. In view of this and since we are a teaching institution working mostly with graduate students it was decided not to run a test using butadiene at this time.

References

1) C. Wey, "Soot Formation in Gaseous Laminar Diffusion Flames," Ph.D Thesis, School of Aerospace Engineering, Georgia Institute of Technology, Atlanta, GA, Nov. 1984.

2) C. Wey, E. A. Powell and J. I. Jagoda, "The Effect of Temperature on Soot Formation in a Gaseous Diffusion Flame," Chemical and Physical Processes in Combustion, Technical Meeting of the Eastern Section of the Combustion Institute, Atlantic City, NJ, Paper # 7, Dec. 14-16, 1982.

3) C. Wey, E. A. Powell and J. I. Jagoda, "The Effect of Temperature on the Sooting Behavior of Laminar Diffusion Flames," Comb. Sci. and Tech., Vol. 41, pt. 3 & 4, pp 173-190, 1984.

4) C. Wey, E. A. Powell and J. I. Jagoda, "The Effect on Soot Formation of Oxygen in the Fuel of a Diffusion Flame," 20th Symposium (International) on Combustion, Ann Arbor, MI, Aug. 1984, in print.